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(54)【発明の名称】　プロトン伝導性膜又はフィルムとそれらを用いてなる燃料電池

(57)【要約】　（修正有）
【課題】耐久性と機械的強度を有するプロトン伝導性膜又はフィルムとそれらの製造方法、更には、それらをプロトン交換膜として用いてなる燃料電池を提供する。
【解決手段】プロトン伝導性膜は、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーとを多孔質膜の空孔内で重合させて、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させることによって得ることができる。上記プロトン伝導性膜の空孔の残余の空隙の少なくとも一部が閉塞されてなるプロトン伝導性フィルムとその製造方法が提供される。上記のほか、上記プロトン伝導性フィルムをプロトン交換膜として用いてなる燃料電池が提供される。

【特許請求の範囲】

【請求項１】側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを多孔質膜の空孔内に担持させてなることを特徴とするプロトン伝導性膜。

【請求項２】多孔質膜が超高分子量ポリオレフィン樹脂又はフッ素樹脂からなるものである請求項１に記載のプロトン伝導性膜。

【請求項３】ポリマーが架橋構造を有する請求項１に記載のプロトン伝導性膜。

【請求項４】請求項１から３のいずれかに記載のプロトン伝導性膜の空孔の残余の空隙の少なくとも一部が閉塞されてなるプロトン伝導性フィルム。

【請求項５】側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーとを多孔質膜の空孔内で重合させて、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させることを特徴とするプロトン伝導性膜の製造方法。

【請求項６】請求項５に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーと共に、リン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない単官能性モノマーを用いるプロトン伝導性膜の製造方法。

【請求項７】請求項５に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーと共に、リン酸基、ホスホン酸基又はホスフィン酸基を有する多官能性モノマー及び／又はリン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない多官能性モノマーを用いて、一部、アミン塩化されたポリマーに架橋構造を有せしめるプロトン伝導性膜の製造方法。

【請求項８】側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーを多孔質膜の空孔内で重合させて、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有するポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させ、更に、このポリマーの上記側鎖のリン酸基、ホスホン酸基又はホスフィン酸基を一部、アミン塩化することを特徴とするプロトン伝導性膜の製造方法。

【請求項９】請求項８に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと共に、リン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない単官能性モノマーを用いるプロトン伝導性膜の製造方法。

【請求項１０】請求項８に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと共に、リン酸基、ホスホン酸基又はホスフィン酸基を有する多官能性モノマー及び／又はリン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない多官能性モノマーを用いて、ポリマーに架橋構造を有せしめるプロトン伝導性膜の製造方法。

【請求項１１】多孔質膜が超高分子量ポリオレフィン樹脂又はフッ素樹脂からなるものである請求項５から１０のいずれか記載のプロトン伝導性膜の製造方法。

【請求項１２】側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーとを含むモノマー混合物を多孔質膜の空孔内で重合させて、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させて、プロトン伝導性膜を得、次いで、このプロトン伝導性膜の空孔の残余の空隙の少なくとも一部を閉塞することを特徴とするプロトン伝導性フィルムの製造方法。

【請求項１３】請求項１２に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーと共に、リン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない単官能性モノマーを用いるプロトン伝導性フィルムの製造方法。

【請求項１４】請求項１２に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーと共に、リン酸基、ホスホン酸基又はホスフィン酸基を有する多官能性モノマー及び／又はリン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない多官能性モノマーを用いて、一部、アミン塩化されたポリマーに架橋構造を有せしめるプロトン伝導性フィルムの製造方法。

【請求項１５】側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーを多孔質膜の空孔内で重合させて、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有するポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させ、更に、このポリマーの上記側鎖のリン酸基、ホスホン酸基又はホスフィン酸基を一部、アミン塩化して、プロトン伝導性膜を得、次いで、このプロトン伝導性膜の空孔の残余の空隙の少なくとも一部を閉塞することを特徴とするプロトン伝導性フィルムの製造方法。

【請求項１６】請求項１５に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する

単官能性モノマーと共に、リン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない単官能性モノマーを用いるプロトン伝導性フィルムの製造方法。

【請求項１７】請求項１５に記載の方法において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと共に、リン酸基、ホスホン酸基又はホスフィン酸基を有する多官能性モノマー及び／又はリン酸基、ホスホン酸基及びホスフィン酸基のいずれをも有しない多官能性モノマーを用いて、ポリマーに架橋構造を有せしめるプロトン伝導性フィルムの製造方法。

【請求項１８】多孔質膜が超高分子量ポリオレフィン樹脂又はフッ素樹脂からなるものである請求項１２から１７のいずれかに記載のプロトン伝導性フィルムの製造方法。

【請求項１９】請求項１から３のいずれかに記載のプロトン伝導性膜をプロトン交換膜として用いてなる燃料電池。

【請求項２０】請求項４に記載のプロトン伝導性フィルムをプロトン交換膜として用いてなる燃料電池。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、プロトン伝導性を有するプロトン伝導性膜、これより得られるプロトン伝導性フィルムとそれらの製造方法、更には、それらプロトン伝導性膜又はフィルムをプロトン交換膜として用いてなる燃料電池に関する。

【０００２】

【従来の技術】従来、プロトン伝導性膜は、イオン交換膜や湿度センサー等の用途に用いられているが、近年、固体高分子型燃料電池における固体電解質膜としての用途においても注目を集めている。例えば、デュポン社のナフィオン（登録商標）を代表とするスルホン酸基含有フッ素樹脂膜は、電気自動車や分散型電源用燃料電池における固体電解質としての利用が検討されているが、従来より知られているこれらのフッ素樹脂系プロトン伝導性膜は、価格が非常に高いという欠点がある。プロトン伝導性膜を燃料電池等の新たな用途において実用化を図るには、プロトン伝導性を高く、しかも価格を低くすることが不可欠である。

【０００３】そこで、従来、空孔を有する多孔質膜に電解質ポリマーを含有させて、プロトン伝導性膜を得る方法が種々提案されている。例えば、特開平９－１９４６０９号公報には、フッ素樹脂、ポリエチレン樹脂、ポリプロピレン樹脂等の疎水性樹脂からなる多孔質膜の空孔内に同じく疎水性のポリマーの溶液を含浸させ、乾燥させて、上記ポリマーを多孔質膜に担持させた後、このポリマーにスルホン酸基、プロトン化アミノ基、カルボキシル基等のイオン交換基を導入し、かくして、イオン交換膜を製造する方法が提案されている。しかし、このような方法によれば、イオン交換基を多孔質膜中に均一に分布させることは困難であり、延いては、プロトン伝導性も十分ではない。

【０００４】そこで、最近、イオン交換基としてリン酸エステル基を有するポリマー、即ち、側鎖にリン酸エステル基を有するメタクリル酸誘導体から導かれるポリマーを固体高分子型燃料電池用プロトン交換膜として用いることが「高分子学会予稿集」第４８巻第３号第４１４頁（１９９９年）、「高分子学会予稿集」第４８巻第１０号第２３９３頁（１９９９年）、「高分子学会予稿集」第４９巻第４号第７５１頁（２０００年）等に提案されている。

【０００５】これら文献によれば、側鎖にリン酸エステル基を有するメタクリル酸誘導体から導かれるポリマーは、上記リン酸エステル基のプロトン解離度が大きく、強い酸性を示すので、高いプロトン伝導性を有しており、しかも、主鎖が炭化水素でありながら、耐熱性を有すると共に、水に殆ど溶解しないという特性を有する。このように、リン酸エステル基を置換基として側鎖に有するポリマーが水不溶性であるのは、リン酸エステル基がそれぞれの間に形成する水素結合によって、ポリマー鎖間に強いネットワークが形成されるためであるとみられる。

【０００６】しかしながら、側鎖にリン酸エステル基を有するメタクリル酸誘導体から導かれる上記ポリマー自体は、機械的強度が低く、脆いので、燃料電池用プロトン交換膜として用いることは困難である。また、上記ポリマーは、その製造時にしばしばゲル化したり、また、得られたポリマーが溶解性に乏しい等、実用化のためには、製造面や成形性の面で尚、多くの問題がある。

【０００７】一般に、多孔質膜にプロトン伝導性を付与するためには、膜内にプロトン発生源又は輸送サイトを有することが必要であり、先に言及したスルホン酸基はそのようなプロトン発生源又は輸送サイトの代表例である。しかし、スルホン酸基を有するポリマーは、代表的には、ポリスチレンスルホン酸やポリビニルスルホン酸等であり、これらはすべて水溶性である。従って、水素ガスや酸素ガスを水蒸気加湿して用いる燃料電池のプロトン交換膜としては、これらのポリマーは、そのままでは、用いることが困難である。即ち、燃料電池のプロトン交換膜として用いるには、ポリマーに何らかの水不溶性化処理を施すことが必要である。

【０００８】水溶性ポリマーを水不溶化するためには、架橋処理をするか、又はスルホン酸基を有するモノマーと共に水不溶性ポリマーを与えるようなモノマーと共重合を行なって、共重合体とする必要がある。

【０００９】しかし、水溶性ポリマーに架橋処理を施すことによって、水に完全に溶解することは避けることができても、水に接触したとき、ポリマーが膨潤することは避けられない。かくして、水溶性ポリマーの架橋による水不溶化は、それと引換えにポリマーの機械的強度の

低下をもたらすので、そのように、水溶性ポリマーを水不溶化したポリマーを燃料電池用プロトン交換膜として用いることも困難である。

【００１０】他方、水不溶性ポリマーを与えるモノマーとの共重合によって、水不溶性ポリマーを得るには、重合に供するモノマー中のスルホン酸基含有モノマーの割合を相対的に低くせざるを得ず、そうすれば、本来、プロトン交換膜として求められるプロトン伝導性が損なわれるので、高いプロトン伝導性を有するポリマーを得ることはできない。

【００１１】

【発明が解決しようとする課題】本発明は、プロトン伝導性膜又はフィルムにおける上述した問題を解決するためになされたものであって、耐久性と機械的強度を有するプロトン伝導性膜又はフィルムとそれらの製造方法、更には、それらをプロトン交換膜として用いてなる燃料電池を提供することを目的とする。

【００１２】

【問題を解決するための手段】本発明によれば、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを多孔質膜の空孔内に担持させてなることを特徴とするプロトン伝導性膜が提供される。

【００１３】更に、本発明によれば、上記プロトン伝導性膜の空孔の残余の空隙の少なくとも一部が閉塞されてなるプロトン伝導性フィルムが提供される。

【００１４】また、本発明によれば、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーとを多孔質膜の空孔内で重合させて、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させることを特徴とするプロトン伝導性膜の製造方法が提供される。

【００１５】更に、本発明によれば、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーを多孔質膜の空孔内で重合させて、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有するポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させ、更に、このポリマーの上記側鎖のリン酸基、ホスホン酸基又はホスフィン酸基を一部、アミン塩化することを特徴とするプロトン伝導性膜の製造方法が提供される。

【００１６】また、本発明によれば、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーとを含むモノマー混合物を多孔質膜の空孔内で重合させて、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させて、プロトン伝導性膜を得、次いで、このプロトン伝導性膜の空孔の残余の空隙の少なくとも一部を閉塞することを特徴とするプロトン伝導性フィルムの製造方法が提供される。

【００１７】更に、本発明によれば、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーを多孔質膜の空孔内で重合させて、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有するポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させ、更に、このポリマーの上記側鎖のリン酸基、ホスホン酸基又はホスフィン酸基を一部、アミン塩化して、プロトン伝導性膜を得、次いで、このプロトン伝導性膜の空孔の残余の空隙の少なくとも一部を閉塞することを特徴とするプロトン伝導性フィルムの製造方法が提供される。

【００１８】上記のほか、本発明によれば、上記プロトン伝導性膜又はプロトン伝導性フィルムをプロトン交換膜として用いてなる燃料電池が提供される。

【００１９】

【発明の実施の形態】本発明によるプロトン伝導性膜は、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを多孔質膜の空孔内に担持させてなるものである。

【００２０】以下、本発明において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有するポリマーを「Ｐ－ポリマー」といい、上記側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを「Ｐ－ポリマーの部分アミン塩」という。

【００２１】本発明によれば、このようなプロトン伝導性膜は、好ましくは、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーと側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーを多孔質膜の空孔内で重合させて、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基が一部、アミン塩化されたポリマーを生成させると共に、このポリマーを上記多孔質膜の空孔内に担持させることによって得ることができる。

【００２２】以下、本発明において、側鎖にリン酸基、ホスホン酸基又はホスフィン酸基を有する単官能性モノマーを「Ｐ－モノマー」といい、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基がアミン塩化された単官能性モノマーを「Ｐ－塩モノマー」という。また、上記リン酸基、ホスホン酸基又はホスフィン酸基を「Ｐ－酸基」という。

【００２３】また、Ｐ－塩モノマーとＰ－モノマーとの混合物を「Ｐ－モノマーの部分アミン塩」という。

【００２４】本発明によるプロトン伝導性膜において、基材として用いる多孔質膜は、特に、限定されることなく、種々の樹脂からなるものを用いることができる。そ

のような樹脂として、例えば、ポリテトラフルオロエチレン等のフッ素樹脂、６，６－ナイロンほか、種々のポリアミド樹脂、ポリエチレンテレフタレート等のポリエステル樹脂、ジメチルフェニレンオキサイド、ポリエーテルエーテルケトン等のポリエーテル樹脂、エチレン、プロピレン等のα－オレフィン、ノルボルネン等の脂環式不飽和炭化素、ブタジエン、イソプレン等の共役ジエン等の（共）重合体、例えば、ポリエチレン樹脂、ポリプロピレン樹脂や、また、エチレン－プロピレンゴム、ブタジエンゴム、イソプレンゴム、ブチルゴム、ノルボルネンゴム等のエラストマーやそれらの水添物等の脂肪族炭化水素樹脂を挙げることができる。これらの樹脂は、単独で、又は２種以上を併用して、上記多孔質膜を形成していてよい。

【００２５】本発明によれば、上記した種々の樹脂からなる多孔質膜のなかでも、ポリオレフィン樹脂、特に、重量平均分子量５．０×１０^5 以上、好ましくは、１．０×１０^6 以上の高分子量ポリエチレン樹脂からなる多孔質膜が強度や耐熱性にすぐれるところから、好ましく用いられる。また、ポリテトラフルオロエチレンやポリフッ化ビニリデン等のフッ素樹脂からなる多孔質膜も、そのすぐれた耐薬品性と耐熱性から、本発明において、好ましく用いられる。

【００２６】本発明によれば、基材多孔質膜は、従来より知られている適宜の手段によって親水化されていてもよい。このような親水化された多孔質膜は、例えば、スルホン酸基、リン酸基、カルボキシル基、アミノ基、アミド基、水酸基等の親水性基を有する重合体やそのブレンドを原料に用いて製膜することによって得ることができる。また、そのような親水性基をもたない重合体を多孔質膜に製膜した後に、その多孔質膜に、例えば、スルホン化処理を施したり、また、界面活性剤を担持させる等の方法によって得ることができる。

【００２７】本発明において、基材多孔質膜は、通常、２０～９０％、好ましくは、３０～８５％の範囲の空孔率を有する。多孔質膜の空孔率が２０％よりも小さいときは、このような多孔質膜の空孔にＰ－ポリマーの部分アミン塩を担持させても、高いプロトン伝導性を有する膜を得ることができない。しかし、多孔質膜の空孔率が９０％よりも大きいときは、そのような多孔質膜の空孔にＰ－ポリマーの部分アミン塩を担持させて得られるプロトン伝導性膜は、強度が十分でなく、取り扱いや種々の用途での使用に困難が伴う。

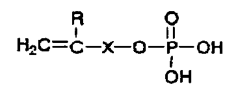
【００２８】また、基材多孔質膜は、Ｐ－ポリマーの部分アミン塩を多孔質膜中に保持することができれば、特に、限定されるものではないが、その平均孔径は、通常、０．００１～１００μｍの範囲であり、０．００５～１０μｍの範囲にあることが好ましい。同様に、多孔質膜の厚みも、特に、限定されるものではないが、通常、１ｍｍ以下であり、好ましくは、５～５００μｍの範囲である。

【００２９】本発明によるプロトン伝導性膜は、好ましくは、Ｐ－モノマーの部分アミン塩を多孔質膜に含浸させ、この多孔質膜の空孔内で重合させて、Ｐ－ポリマーの部分アミン塩を生成させると共に、このＰ－ポリマーの部分アミン塩を上記多孔質膜の空孔内に担持させることによって得ることができる。

【００３０】本発明によれば、上記Ｐ－モノマーのうち、リン酸基を有するモノマーの好ましい例として、一般式（Ｉ）

【００３１】

【化１】



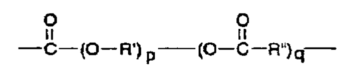
(I)

【００３２】（式中、Ｒは水素原子又はメチル基を示し、Ｘは基の両末端が炭素原子である２価の有機基を示す。）で表わされる化合物を挙げることができる。

【００３３】特に、本発明においては、上記基Ｘは、好ましくは、一般式（Ａ）

【００３４】

【化２】



(A)

【００３５】（式中、Ｒ’はエチレン基又はプロピレン基を示し、Ｒ”は炭素原子数１～１０、好ましくは、２～６の直鎖状又は分岐鎖状アルキレン基を示し、ｐは１～１０の整数であり、ｑは０、１又は２である。）で表わされる２価基か、又は一般式（Ｂ）

【００３６】

【化３】

$$—Ar—CH_2—[O—R'''—(Ar')_s]_r—$$

(B)

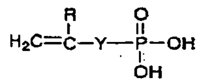
【００３７】（式中、Ａｒ及びＡｒ’はそれぞれ独立に２価の芳香族炭化水素基、好ましくは、フェニレン基を示し、Ｒ'"は炭素原子数１～１０、好ましくは、２～６の直鎖状又は分岐鎖状アルキレン基を示し、ｒは０又は１であり、ｒが１のとき、ｓは０又は１である。）で表わされる２価基を示す。

【００３８】従って、上記一般式（Ｉ）で表わされるＰ－モノマーの好ましい具体例としては、例えば、２－メタクリロイルオキシエチルホスフェート、メタクリロイルテトラ（オキシエチレン）ホスフェート、メタクリロイルペンタ（オキシプロピレン）ホスフェート、４－スチリルメトキシブチルホスフェート等を挙げることができる。

【００３９】ホスホン酸基を有するモノマーの好ましい例としては、一般式（II）

【００４０】

【化４】



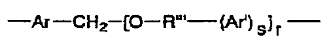
(II)

【００４１】（式中、Ｒは水素原子又はメチル基を示し、Ｙは基の両末端が炭素原子である２価の有機基を示す。）で表わされる化合物を挙げることができる。

【００４２】特に、本発明においては、上記基Ｙは、好ましくは、一般式（Ｂ）

【００４３】

【化５】



(B)

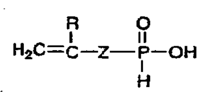
【００４４】（式中、Ａｒ及びＡｒ’はそれぞれ独立に２価の芳香族炭化水素基、好ましくは、フェニレン基を示し、Ｒ’"は炭素原子数１～１０、好ましくは、２～６の直鎖状又は分岐鎖状アルキレン基を示し、ｒは０又は１であり、ｒが１のとき、ｓは０又は１である。）で表わされる２価基を示す。

【００４５】従って、上記一般式（II）で表わされるホスホン酸基を有するモノマーの好ましい具体例としては、例えば、４－（２－スチリルメトキシエチル）フェニルホスホン酸、４－（スチリルメトキシ）ブチルホスホン酸、スチリルメチルホスホン酸等の化合物を挙げることができる。

【００４６】また、ホスフィン酸基を有するモノマーの好ましい例としては、一般式（III）

【００４７】

【化６】



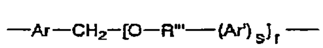
(III)

【００４８】（式中、Ｒは水素原子又はメチル基を示し、Ｚは基の両末端が炭素原子である２価の有機基を示す。）で表わされる化合物を挙げることができる。

【００４９】特に、本発明においては、上記基Ｚは、好ましくは、一般式（Ｂ）

【００５０】

【化７】



(B)

【００５１】（式中、Ａｒ及びＡｒ’はそれぞれ独立に２価の芳香族炭化水素基、好ましくは、フェニレン基を示し、Ｒ’"は炭素原子数１～１０、好ましくは、２～６の直鎖状又は分岐鎖状アルキレン基を示し、ｒは０又は１であり、ｒが１のとき、ｓは０又は１である。）で表わされる２価基を示す。

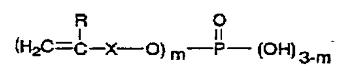
【００５２】従って、上記一般式（III)で表わされるホスフィン酸基を有するモノマーの具体例としては、例えば、４－（２－スチリルメトキシエチル）フェニルホスフィン酸、４－（スチリルメトキシ）ブチルホスフィン酸、スチリルメチルホスフィン酸等の化合物を挙げることができる。

【００５３】本発明によれば、Ｐ－ポリマーの部分アミン塩の製造において、Ｐ－モノマーの部分アミン塩と共に、Ｐ－酸基を有する多官能性モノマー（以下、多官能性Ｐ－モノマーということがある。）を用いることができる。

【００５４】このような多官能性Ｐ－モノマーの好ましい例として、例えば、一般式（IV）

【００５５】

【化８】



(IV)

【００５６】（式中、ＲとＸは前記と同じであり、ｍは２又は３である。）で表わされるリン酸ジエステル又はトリエステルを挙げることができる。

【００５７】本発明においては、このような多官能性Ｐ－モノマーのうち、特に、基Ｘが前記一般式（Ａ）で表わされる基であるものが好ましい。

【００５８】従って、このような多官能性Ｐ－モノマーの具体例として、例えば、ビス（メタクリロイルオキシエチル）ホスフェート、ビス｛５－（メタクリロイルオキシエチルオキシカルボニル）ペンチル｝ホスフェート等のリン酸ジエステルを挙げることができる。

【００５９】Ｐ－モノマーの部分アミン塩がこのような多官能性Ｐ－モノマーを含むとき、この多官能性Ｐ－モノマーの割合は５０モル％以下であり、好ましくは、４５モル％以下である。

【００６０】このように、Ｐ－モノマーの部分アミン塩と共に多官能性Ｐ－モノマーを用いることによって、得られるＰ－ポリマーの部分アミン塩は、上記多官能性Ｐ－モノマーの架橋反応によって、三次元構造、即ち、架橋構造を有し、かくして、Ｐ－ポリマーの部分アミン塩の耐水性や耐溶剤性等の物性を更に改善することができる。

【００６１】また、本発明によれば、Ｐ－モノマーの部分アミン塩と共に、Ｐ－酸基のいずれをも有しない多官能性モノマー（以下、多官能性非Ｐ－モノマーということがある。）を用いることができる。このように、Ｐ－モノマー部分アミン塩が多官能性非Ｐ－モノマーを含む

とき、この多官能性非Ｐ－モノマーの割合は５０モル％以下であり、好ましくは、４５モル％以下である。

【００６２】このように、Ｐ－モノマーの部分アミン塩と共に多官能性非Ｐ－モノマーを用いることによって、得られるＰ－ポリマーの部分アミン塩は、種々の物性、例えば、ガラス転移温度、親水性の程度、柔軟性、機械的強度等を調整することもできる。

【００６３】しかし、本発明によるプロトン伝導性膜において、Ｐ－ポリマーの部分アミン塩に架橋構造をもたせるための手段は、上記に限定されるものではなく、例えば、官能基間の反応、過酸化物による架橋、電子線等の照射、オゾンの作用等、従来より知られている適宜の手段を利用することができる。

【００６４】更に、本発明によれば、Ｐ－モノマーの部分アミン塩と共に、Ｐ－酸基のいずれをも有しない単官能性モノマー（以下、単官能性非Ｐ－モノマーということがある。）を用いて、Ｐ－モノマーの部分アミン塩と共重合体を形成させてもよい。

【００６５】このような単官能性非Ｐ－モノマーとしては、例えば、スチレン、ビニルスルホン酸、スチレンスルホン酸ナトリウム等のビニルモノマー類、エチルビニルエーテル等のビニルエーテル類、アクリル酸ブチル、メトキシエチルアクリレート、２－エチルヘキシルメタクリレート、アクリル酸等のアクリルモノマー類、Ｎ，Ｎ－ジメチルアミノプロピルアクリルアミド、２－アクリルアミド－２－メチルプロパンスルホン酸等のアクリルアミド類を挙げることができる。

【００６６】本発明において、Ｐ－モノマーの部分アミン塩（多官能性Ｐ－モノマーを含む。）と共に単官能性非Ｐ－モノマーを用いる場合、その単官能性非Ｐ－モノマーの割合は、用いる基材多孔質膜の空孔率にもよるが、通常、Ｐ－モノマーの部分アミン塩（多官能性Ｐ－モノマーを含む。）に対して、９０モル％以下の範囲であり、好ましくは、８０モル％以下の範囲である。単官能性非Ｐ－モノマーの割合がＰ－モノマーの部分アミン塩（多官能性Ｐ－モノマーを含む。）に対して９０モル％よりも多いときは、高プロトン伝導性膜を得ることができない。

【００６７】本発明において、Ｐ－モノマーのＰ－酸基をアミン塩化するには、即ち、Ｐ－酸基がアミン塩化されたＰ－モノマーを得るには、Ｐ－モノマーにアミンを作用させる。

【００６８】ここに、上記アミンは、特に、限定されるものではないが、例えば、ピリジン、キノリン、アクリジン、イミダゾール、ピラゾール、ピペリジン、ピペラジン等の複素環式アミンやその誘導体、アニリン、トルイジン、ベンジルアミン、ジフェニルアミン、ナフチルアミン等の芳香族アミンやその誘導体、ｎ－ブチルアミン、ｎ－ヘキシルアミン等の脂肪族アミンやその誘導体、モノエタノールアミン、ジエタノールアミン等のアルカノールアミン、グリシン、グルタミン酸等のアミノ酸、ベタイン等の両性物質等を挙げることができる。

【００６９】本発明によれば、前記Ｐ－モノマーの部分アミン塩は、好ましくは、アミンのアミノ基／Ｐ－モノマーの有するＰ－酸基の比率Ｒが０＜Ｒ＜１となるように、Ｐ－モノマーにアミンを作用させて、アミン塩化していないＰ－モノマーとアミン塩化したＰ－モノマーとの混合物として得ることができる。特に、本発明によれば、Ｐ－モノマーの部分アミン塩において、アミンのアミノ基／Ｐ－モノマーの有するＰ－酸基の比率Ｒは、０．１≦Ｒ≦０．９の範囲であることが好ましい。

【００７０】しかし、本発明によれば、Ｐ－モノマーをすべて、アミン塩化し、このアミン塩化Ｐ－モノマーと、アミン塩化していないＰ－モノマーとを混合し、これをＰ－モノマーの部分アミン塩とすることもできる。従って、この場合には、アミン塩化したＰ－モノマーとアミン塩化していないＰ－モノマーにおいて、それぞれのＰ－モノマーは同じでもよく、異なっていてもよい。

【００７１】本発明によれば、かくして、プロトン伝導性膜は、好ましくは、Ｐ－モノマーの部分アミン塩と、必要に応じて、上述した多官能性Ｐ－モノマーや多官能性非Ｐ－モノマー、単官能性非Ｐ－モノマー等、Ｐ－モノマーやＰ－塩モノマーと共重合性を有するモノマーを基材多孔質膜に担持させ、熱重合や光重合等、従来より知られている適宜の方法によって、上記モノマーを重合させればよい。しかし、重合法としては、なかでも、光重合法が簡便で安全あり、しかも、短時間でＰ－ポリマーの部分アミン塩を得ることができる。また、光重合を行なった後、必要に応じて、残余のモノマーを重合させるために、より高温で更に光重合や熱重合を行なってもよい。

【００７２】上記光重合開始剤は、従来より知られているものを適宜に用いればよい。例えば、２－ベンジル－２－ジメチルアミノ－１－（４－モルホリノフェニル）ブタノン－１（チバガイギー社製イルガキュア３６９）、２－メチル－１－｛４－（メチルチオ）フェニル｝－２－モルホリノプロパノン－１（チバガイギー社製イルガキュア９０７）、１－ヒドロキシシクロヘキシルフェニルケトン（チバガイギー社製イルガキュア１８４）、ベンジルジメチルケタール（チバガイギー社製イルガキュア６５１）等を用いることができる。３００ｎｍ以上の波長の光を用いても重合が可能であるものが特に好ましい。このような光重合開始剤は、通常、Ｐ－モノマーの部分アミン塩を含むモノマー全体に対して０．０１～５重量％程度加えられる。

【００７３】Ｐ－モノマーの部分アミン塩や、必要に応じて、前記その他の共重合性モノマーや、光重合開始剤等を含む混合物を多孔質膜の空孔内に担持させるためには、例えば、この混合物に多孔質膜を浸漬したり、また、この混合物を基材多孔質膜に塗布すればよい。

【００７４】このように、Ｐ－モノマーの部分アミン塩やそれを含む混合物を多孔質膜に担持させるに際して、このＰ－モノマー部分アミン塩やそれを含む混合物の粘度を適宜に調整してもよい。即ち、粘度を高めるためにＰ－モノマーの部分アミン塩の一部を予備重合させたり、また、適宜のポリマーを少量、添加し、溶解させてもよい。反対に、粘度を下げるために、適当な溶剤を加えて、希釈してもよい。

【００７５】このようにして、多孔質膜にＰ－モノマーの部分アミン塩やこれを含む混合物を担持させた後、例えば、ポリエステル樹脂製離型フィルムで多孔質膜を挟み、この交換膜を酸素（従って、例えば、空気）から遮断して、高圧水銀ランプ等を用いてＰ－モノマーの部分アミン塩やその他の共重合性モノマーに光照射し、光重合させることによって、Ｐ－ポリマーの部分アミン塩を多孔質膜の空孔内に担持させてなるプロトン伝導性膜を得ることができる。

【００７６】上記光重合に必要な光照射量は、系により異なるが、通常は、０．１～５Ｊ／ｃm^2 程度で十分である。光重合は、得られるＰ－ポリマーの部分アミン塩の分子量を高くするために、通常、室温付近で行なうが、しかし、重合率を高めるために、より高い温度で光重合を行なってもよい。また、最初は低温で、次いで、高温で光重合してもよい。

【００７７】また、別の方法として、本発明によるプロトン伝導性膜は、Ｐ－モノマーを多孔質膜の空孔内で前述したと同様にして重合させて、Ｐ－ポリマーを生成させ、次いで、このＰ－ポリマーにアミンを作用させて、そのＰ－酸基の一部をアミン化することによっても得ることができる。本発明によれば、この場合、アミンのアミノ基／Ｐ－ポリマーの有するＰ－酸基の比率Ｒが０＜Ｒ＜１となるように、アミンをＰ－ポリマーに作用させ、好ましくは、アミンのアミノ基／Ｐ－ポリマーの有するＰ－酸基の比率Ｒが０．１≦Ｒ≦０．９となるように、アミンをＰ－ポリマーに作用させる。

【００７８】このように、Ｐ－モノマーを多孔質膜の空孔内で重合させて、Ｐ－ポリマーを生成させる場合にも、Ｐ－モノマーの部分アミン塩を重合させる場合と同様に、多官能性Ｐ－モノマーや多官能性非Ｐ－モノマーを必要に応じて用いて、架橋構造を有するＰ－ポリマーを架橋させ、また、単官能性Ｐ－モノマーを用いて、それとの共重合体を生成させることができる。

【００７９】本発明によれば、Ｐ－モノマーの部分アミン塩又はＰ－モノマー、必要に応じて、これらに共重合性を有する前記その他のモノマーとのモノマー混合物を多孔質膜に含浸させる際、多孔質膜の空孔を上記モノマー混合物が充填する比率（充填率）が低いときは、上記モノマーの重合後も、基材多孔質膜は、通気性を有する多孔質構造を有しており、かくして、（必要な場合には、生成したＰ－ポリマーのＰ－酸基をアミン塩化して、）通気性を有するプロトン伝導性多孔質膜を得ることができる。他方、上記充填率が高いときは、上記モノマーの重合後、基材多孔質膜は、その空孔が実質的に閉塞されて、（必要な場合には、生成したＰ－ポリマーのＰ－酸基をアミン塩化して、）通気性のないプロトン伝導性無孔膜を得ることができる。一応の目安として、モノマーの充填率が８０％以上であれば、基材多孔質膜の空孔が実質的に閉塞されてなる通気性のないプロトン伝導性無孔膜を得ることができる。

【００８０】本発明においては、Ｐ－モノマーの部分アミン塩やＰ－モノマー、これらに共重合性を有する上記その他のモノマーとのモノマー混合物は、基材多孔質膜の空孔を充填するのみならず、基材多孔質膜の少なくとも一方の表面の少なくとも一部を被覆していてもよい。この場合、上記モノマー混合物の充填率は１００％を越える。このように、基材多孔質膜にモノマー混合物を１００％を越える充填率で担持させ、これに光照射すれば、多孔質膜は、その空孔が生成するポリマーで充填されているのみならず、（必要な場合には、生成したＰ－ポリマーのＰ－酸基をアミン塩化して、）少なくとも一方の表面の少なくとも一部がそのポリマーで被覆されたプロトン伝導性膜を得ることができる。

【００８１】更に、本発明によれば、このようにして得られたプロトン伝導性膜の有する空孔の残余の空隙、即ち、このようにして得られたプロトン伝導性膜に残存する空隙を加熱、収縮させ、又は加熱、溶融させる等の適宜手段によって、プロトン伝導性膜に残存する上記空隙の少なくとも一部を閉塞して、プロトン伝導性フィルムとすることができ、特に、好ましくは、プロトン伝導性膜に残存する空隙をすべて閉塞して、通気性のないプロトン伝導性無孔フィルムを得ることができる。また、必要に応じて、プロトン伝導性膜に残存する空隙を一部閉塞して、通気性のあるプロトン伝導性有孔フィルムを得ることができる。

【００８２】このように、Ｐ－ポリマーの部分アミン塩を基材多孔質膜の空孔内に担持させてなるプロトン伝導性膜やプロトン伝導性フィルムは、高いプロトン伝導性を有する。本発明によれば、多孔質膜へのＰ－モノマーの部分アミン塩やこれを含むモノマー混合物の充填率を高くして、多孔質膜の有する空孔へのＰ－ポリマーの部分アミン塩の充填率を高くするほど、高いプロトン伝導性を有する膜やフィルムを得ることができる。

【００８３】本発明によれば、このように、多孔質構造を有し、通気性を有するプロトン伝導性膜や、反対に、無孔構造のプロトン伝導性膜を得ることができ、また、多孔質構造を有し、通気性を有するプロトン伝導性フィルムや、反対に、無孔構造のプロトン伝導性フィルムを得ることができる。多孔質構造を有し、通気性を有するプロトン伝導性膜やフィルムは、例えば、選択透過性荷電膜等、その空隙を活かした用途に好ましく用いること

ができる。

【００８４】しかし、多孔質構造を有し、通気性を有するプロトン伝導性膜やフィルムは、燃料電池用セパレーターとして用いれば、ガスのクロスリークが起こりやすい等の問題がある。従って、このような用途には、上述したように、多孔質膜の空孔を実質的にすべてＰ－ポリマーの部分アミン塩で充填したプロトン伝導性無孔膜を用いたり、また、プロトン伝導性多孔質膜を前述したように加熱、溶融させる等の適宜の手段によって、プロトン伝導性膜に残存する空隙をすべて閉塞してなるプロトン伝導性無孔フィルムを用いることが好ましい。

【００８５】本発明によるプロトン伝導性膜やプロトン伝導性フィルムは、Ｐ－ポリマーの部分アミン塩からなるプロトン伝導性ポリマーを多孔質膜に複合化したものであり、好ましくは、Ｐ－モノマーの部分アミン塩を多孔質膜に含浸させ、この多孔質膜の空孔内で重合させて、Ｐ－ポリマーの部分アミン塩を生成させると共に、このＰ－ポリマーの部分アミン塩を上記多孔質膜の空孔内に担持させて、多孔質膜とＰ－ポリマーの部分アミン塩とを一体化したものである。

【００８６】従って、本発明によれば、基材多孔質膜とプロトン伝導性ポリマーとの複合化に由来して、種々の点ですぐれたプロトン伝導性膜又はフィルムを得ることができる。例えば、超高分子量ポリエチレン等からなる強靭な多孔質膜を基材として用いることによって、Ｐ－ポリマーの部分アミン塩に由来する高いプロトン伝導性に加えて、高い機械的強度とすぐれたハンドリング性を有するプロトン伝導性膜又はフィルムを得ることができる。

【００８７】特に、本発明に従って、Ｐ－モノマーの部分アミン塩を多孔質膜の空孔内に担持させ、重合させて、Ｐ－ポリマーの部分アミン塩を基材多孔質膜と一体化することによって、Ｐ－ポリマーの部分アミン塩のポリマー鎖を多孔質膜の網目に高度に絡みつかせることができ、更には、Ｐ－モノマーの部分アミン塩と共に多官能性Ｐ－モノマーや多官能性非Ｐ－モノマーを共重合させれば、架橋したＰ－ポリマーの部分アミン塩と多孔質膜を構成するポリマー鎖とが相互貫通したポリマーネットワークによって物理的な結合が生じ、かくして、プロトン伝導性ポリマーと多孔質膜との密着性を一層強めたプロトン伝導性膜やフィルムを得ることができる。

【００８８】

【実施例】以下に実施例を挙げて本発明を説明するが、本発明はこれら実施例により何ら限定されるものではない。また、以下において、用いた多孔質膜の特性や、得られたプロトン伝導性膜又はフィルムの特性は、次のようにして評価した。

【００８９】（膜又はフィルムの厚み）１／１００００シックネスゲージで測定した。

（多孔質膜の空孔率）多孔質膜の単位面積Ｓ（ｃｍ^2）あたりの重量Ｗ（ｇ）、平均厚みｔ（μｍ）及び密度ｄ（ｇ／ｃｍ^3）から下式にて算出した。

【００９０】空孔率（％）＝（１－（１０^4・Ｗ／(Ｓ・ｔ・ｄ)））×１００

【００９１】（プロトン伝導度）プロトン伝導性膜又はフィルムを温度２５℃、相対湿度５０％に調整した環境下に４時間放置した後、ヒューレットパッカード社ＬＣＲメーターＨＰ４２８４Ａを用いて、白金電極間に所定厚みの１ｃｍ角の試料を挟み、温度２５℃、相対湿度５０％の条件下で複素インピーダンス法にて測定し、虚数部の抵抗値ゼロに外挿したときの実数部の抵抗値を用いてプロトン伝導度を算出した。

【００９２】（基材多孔質膜の空孔へのＰ－ポリマーの部分アミン塩の体積充填率）基材多孔質膜の体積Ｖ（ｃｍ^3）、基材多孔質膜の空孔率Φ（％）、Ｐ－ポリマーの部分アミン塩の重量Ｍ（ｇ）及びＰ－ポリマーの部分アミン塩の密度ｄ（ｇ／ｃｍ^3）から下式にて算出した。

【００９３】充填率（％）＝１０^4・Ｍ／（Ｖ・Φ・ｄ）

【００９４】（引張強度）ダンベル型に打ち抜いた試験片（ＪＩＳ　Ｋ　７１１３、プラスチックの引張試験方法における１号形試験片に準拠）について、引張試験機（（株）島津製作所製オートグラフＡＧＳ－５０Ｄ）を用いて測定した。

【００９５】実施例１

（Ｐ－モノマーの部分アミン塩の調製）２－メタクリロイルオキシエチルホスフェート／ビス（メタクリロイルオキシエチル）ジホスフェート（６５／３５モル比）からなるＰ－モノマー（共栄社化学（株）製ライトエステルＰ－１Ｍ）７０重量％とメトキシエチルアクリレート３０重量％とからなるモノマー混合物１００重量部に撹拌しながら、予め、計算した所要量のジエタノールアミンを徐々に加えて、ジエタノールアミンのアミノ基／Ｐ－モノマーのリン酸基の比率Ｒ＝１／２のＰ－モノマーの部分アミン塩とメトキシエチルアクリレートとからなるモノマー混合物を得た。

【００９６】（プロトン伝導性膜の製造）上記モノマー混合物１００重量部にベンジルジメチルケタール（チバガイギー社製イルガキュア６５１）０．２５重量部、１－ヒドロキシシクロヘキシルフェニルケトン（チバガイギー社製イルガキュア１８４）０．２５重量部を溶解させた。

【００９７】これを希釈することなく、そのまま、重量平均分子量１．０×１０^6 の超高分子量ポリエチレン樹脂からなる多孔質膜Ｔ１（膜厚２５μｍ、空孔率４０％、平均孔径０．１０μｍ）の両面に塗布して、多孔質膜の空孔に含浸させた。

【００９８】このように処理した多孔質膜をポリエステル樹脂製離型フィルムで挟んで、多孔質膜を空気から遮

断した後、高圧水銀ランプを備えた光照射装置（アイグラフィック（株）製ＵＢ０２１－１Ｂ－１３）を用いて、上記多孔質膜にエネルギー１．５Ｊ／ｃｍ^2 にて光照射して、その空孔内で上記モノマー混合物を光重合させ、Ｐ－ポリマーの部分アミン塩とメトキシエチルアクリレートとの共重合体を生成させると共に、これを上記多孔質膜の空孔内に担持させて、厚み４０μｍのプロトン伝導性膜Ｆ１を得た。このプロトン伝導性膜においては、多孔質膜の空孔は上記Ｐ－ポリマーの部分アミン塩とメトキシエチルアクリレートとの共重合体にて完全に充填されており、また、多孔質膜の両表面も、上記共重合体の層で被覆されていた。

【００９９】上記プロトン伝導性膜Ｆ１のプロトン伝導度は２．３×１０$^{-3}$ Ｓ／ｃｍであり、引張強度は７５ＭＰａであった。

【０１００】（燃料電池）白金触媒を０．６ｍｇ／ｃｍ^2 の割合で表面に担持させたカーボンペーパー２枚の間に上記プロトン伝導性膜Ｆ１を挟み、ホットプレスを用いて接合して、膜－電極接合体（ＭＥＡ）を製作した。

【０１０１】（株）東陽テクニカ製燃料電池評価装置を用いて、上記ＭＥＡの燃料電池特性を評価した。背圧弁は絞らず、圧力は常圧にて行なった。加湿器温度は水素側８０℃、酸素側７０℃とし、燃料電池セル温度は７０℃とした。Ｔａｆｅｌ法にて電流－電圧（Ｉ－Ｖ）曲線を得たところ、結果を図１に示すように、プロトン交換膜として、ナフィオン（登録商標）１１７膜を用いた場合とほぼ同等の電流－電圧（Ｉ－Ｖ）曲線を得た。即ち、本発明によるプロトン伝導性膜は、ナフィオン１１７膜と同等の燃料電池特性を有する。

【０１０２】実施例２

（Ｐ－モノマーの部分アミン塩の調製）実施例１と同じ２－メタクリロイルオキシエチルホスフェートとビス（メタクリロイルオキシエチル）ジホスフェートとからなるＰ－モノマー１００重量部に撹拌しながら、予め、計算した所要量のイミダゾールの粉末を徐々に加えて、イミダゾールのアミノ基／Ｐ－モノマーのリン酸基の比率Ｒ＝１／３のＰ－モノマーの部分アミン塩とした。

【０１０３】（プロトン伝導性膜の製造）上記Ｐ－モノマーの部分アミン塩１００重量部にベンジルジメチルケタール（前記と同じ）０．２５重量部、１－ヒドロキシシクロヘキシルフェニルケトン（前記と同じ）０．２５重量部を溶解させた。

【０１０４】実施例１と同じ超高分子量ポリエチレン樹脂からなる多孔質膜Ｔ１をポリエステル樹脂製離型フィルム上に載せ、多孔質膜の露出表面に、上記Ｐ－モノマーの部分アミン塩を希釈することなく、そのまま、塗布し、バーでしごいて余剰のモノマーを多孔質膜の表面から除去して、多孔質膜の空孔中にのみ、上記Ｐ－モノマーの部分アミン塩を含浸させた。

【０１０５】このように処理した多孔質膜の露出表面にもポリエステル樹脂製離型フィルムを被せて、多孔質膜を空気から遮断し、実施例１と同じ光照射装置を用いて、エネルギー１．５Ｊ／ｃｍ^2 にて多孔質膜に光照射して、その空孔内で上記Ｐ－モノマーの部分アミン塩を光重合させ、Ｐ－ポリマーの部分アミン塩を生成させると共に、このＰ－ポリマーの部分アミン塩を上記空孔内に担持させて、厚み２５μｍのプロトン伝導性膜Ｆ２を得た。このプロトン伝導性膜においては、多孔質膜の空孔はポリマーにて完全に充填されていた。このプロトン伝導性膜Ｆ２のプロトン伝導度は１．２×１０$^{-3}$ Ｓ／ｃｍであった。

【０１０６】実施例３

（Ｐ－モノマーの部分アミン塩の調製）実施例１と同じ２－メタクリロイルオキシエチルホスフェートとビス（メタクリロイルオキシエチル）ジホスフェートとからなるＰ－モノマー１００重量部に撹拌しながら、予め、計算した所要量のアニリンを徐々に加えて、アニリンのアミノ基／Ｐ－モノマーのリン酸基の比率Ｒ＝１／５のＰ－モノマーの部分アミン塩とした。

【０１０７】（プロトン伝導性膜の製造）上記Ｐ－モノマーの部分アミン塩１００重量部にベンジルジメチルケタール（前記と同じ）０．２５重量部、１－ヒドロキシシクロヘキシルフェニルケトン（前記と同じ）０．５重量部を溶解させ、これをＰ－モノマーの部分アミン塩濃度が３０重量％となるようにメタノールにて希釈した。希釈した。

【０１０８】重量平均分子量２．４×１０^6 の超高分子量ポリエチレン樹脂からなる多孔質膜Ｔ２（膜厚４０μｍ、空孔率４４％、平均孔径0.１５μｍ）をポリエステル樹脂製離型フィルム上に載せ、この多孔質膜の露出表面に、上記Ｐ－モノマーの部分アミン塩混合物の希釈溶液を塗布し、バーでしごいて余剰のモノマーを多孔質膜の表面から除去して、風乾して、多孔質膜の空孔中にのみ、上記Ｐ－モノマーの部分アミン塩を含浸させた。

【０１０９】このように処理した多孔質膜の露出表面にもポリエステル樹脂製離型フィルムを被せて、多孔質膜を空気から遮断し、実施例１と同じ光照射装置を用いて、エネルギー１．５Ｊ／ｃｍ^2 にて多孔質膜に光照射して、その空孔内で上記モノマー混合物を光重合させ、Ｐ－ポリマーの部分アミン塩を生成させると共に、このＰ－ポリマーの部分アミン塩を上記空孔内に担持させて、厚み４０μｍのプロトン伝導性膜Ｆ３を得た。このプロトン伝導性膜においては、多孔質膜の空孔はＰ－ポリマーの部分アミン塩にて部分的に充填されていた。このプロトン伝導性膜Ｆ３のプロトン伝導度は８．５×１０$^{-5}$ Ｓ／ｃｍであった。

【０１１０】比較例１

実施例１において、基材多孔質膜を用いることなく、ポリエステル樹脂製離型フィルム上に実施例１と同じＰ－モノマーの部分アミン塩を含むモノマー混合物を厚み４

０μｍの層に塗布した。

【０１１１】この塗布層の上にもポリエステル樹脂製離型フィルムを載せて、上記モノマー混合物の部分アミン塩の塗布層を空気から遮断し、実施例１と同じ光照射装置を用いて、エネルギー１．５Ｊ／ｃｍ^{2} にて光照射して、Ｐ－ポリマーの部分アミン塩とメトキシエチルアクリレートとの共重合体を生成させて、この共重合体のみからなる厚み４０μｍのプロトン伝導性膜Ｒ１を得た。このプロトン伝導性膜のプロトン電導度は２．６×１０$^{-3}$ Ｓ／ｃｍであり、また、引張強度は、９ＭＰａであった。

【０１１２】比較例２

ポリスチレンスルホン酸ナトリウムの水溶液（東ソー（株）製ポリナスＰＳ－５）を強酸性カチオン交換樹脂を用いてイオン交換し、ナトリウム塩を遊離酸に変換し、これを濃縮した後、メタノールに溶解させて、２０％濃度のポリスチレンスルホン酸のメタノール溶液を調製した。

【０１１３】実施例３と同じ超高分子量ポリエチレン樹脂からなる多孔質膜Ｔ２をポリエステル樹脂製離型フィルムに載せ、その露出表面に上記ポリスチレンスルホン酸のメタノール溶液を塗布し、乾燥させて、厚み５８μｍのプロトン伝導性膜Ｒ２を得た。

【０１１４】このプロトン伝導性膜においては、多孔質膜の空孔は上記ポリスチレンスルホン酸にて完全に充填されており、また、多孔質膜の上記ポリスチレンスルホン酸の塗布側の表面も、ポリスチレンスルホン酸の層で被覆されていた。このプロトン伝導性膜Ｒ２のプロトン伝導度は２．０×１０$^{-5}$ Ｓ／ｃｍであった。

【０１１５】このプロトン伝導性膜を２４時間水に浸漬したところ、ポリスチレンスルホン酸が一部、水中に溶出した結果、この水への浸漬後に再び温度２５℃、相対湿度５０％に調湿してプロトン伝導度を測定したところ、３．７×１０$^{-6}$ Ｓ／ｃｍであった。

【０１１６】

【発明の効果】以上のように、本発明によるプロトン伝導性膜は、側鎖のリン酸基、ホスホン酸基又はホスフィン酸基の一部がアミン塩化されたＰ－ポリマーの部分アミン塩を多孔質膜の空孔内に担持させてなるものであり、高いプロトン伝導性を有するのみならず、高い強度を有し、更に、上記Ｐ－ポリマーの部分アミン塩は水不溶性である。

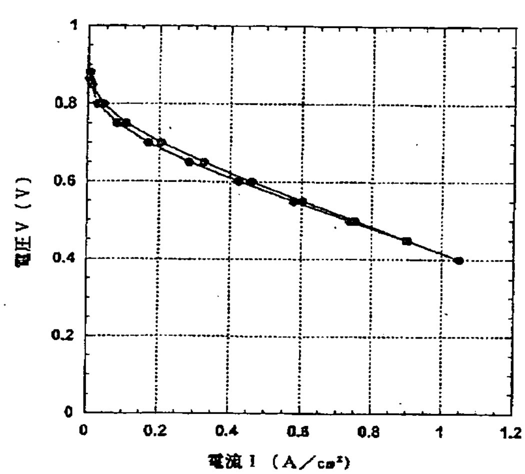
【０１１７】特に、本発明に従って、Ｐ－モノマーの部分アミン塩を多孔質膜の空孔内で重合させて、Ｐ－ポリマーの部分アミン塩を生成させると共に、このＰ－ポリマーの部分アミン塩を上記多孔質膜の空孔内に担持させてなるプロトン伝導性膜によれば、Ｐ－ポリマーの部分アミン塩と多孔質膜が一体化され、Ｐ－ポリマーの部分アミン塩は多孔質膜に対して高度の密着性を有する。しかも、本発明によるプロトン伝導性膜は、従来のスルホン酸基含有フッ素樹脂膜からなるプロトン伝導性膜に比べて格段に低廉に得ることができる。

【０１１８】かくして、本発明によるプロトン伝導性膜は、燃料電池におけるイオン交換膜として好適に用いることができ、ここに、低廉であることから、燃料電池システムのコストを大幅に低減せしめて、その実用化を速めることができる。

【図面の簡単な説明】

【図１】は、本発明によるプロトン伝導性膜を用いて調製した膜－電極接合体（ＭＥＡ）の燃料電池特性を示すＴａｆｅｌ法による電流－電圧（Ｉ－Ｖ）曲線である。

【図１】



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(54) PROTON CONDUCTIVE MEMBRANE OR FILM, AND FUEL CELL USING IT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a proton conductive membrane or film having durability and mechanical strength and its manufacturing method, and to provide a fuel cell using this membrane or film as a proton exchange membrane.
SOLUTION: This proton conductive membrane is obtained by polymerizing a single functional monomer having a phosphate group, a phosphonate group or a phosphinate group in the side and a single functional monomer having an amine salt of the phosphate group, the phosphonate group or the phosphinate group in the side chain, in the void of a porous membrane, by producing a polymer having a part of the phosphate group in the form of an amine salt, the phosphonate group or the phosphinate group in the side chain, and by carrying the polymer in the voids of the porous membrane. The proton conductive film formed by blocking at least a part of the remaining voids of the voids of the proton conductive membrane and the manufacturing method of the proton conductive film are provided. In addition, the fuel cell using the proton conductive film as the proton exchange membrane is provided.

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CLAIMS

[Claim(s)]
[Claim 1] Proton conductivity film with which a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical is characterized by making it come to support the polymer by which amine chlorination was carried out in the hole of porous membrane.
[Claim 2] Proton conductivity film according to claim 1 which is what porous membrane becomes from ultrahigh-molecular-weight polyolefin resin or a fluororesin.
[Claim 3] Proton conductivity film according to claim 1 with which a polymer has the structure of cross linkage.
[Claim 4] The proton conductivity film with which either of claims 1-3 comes to blockade a part of opening [at least] of the remainder of the hole of the proton conductivity film of a publication.
[Claim 5] The phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer by which the amine chlorination of a phosphonic acid radical or the phosphinic acid radical was carried out in the hole of porous membrane and by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out generate The manufacture approach of the proton conductivity film characterized by making this polymer support in the hole of the above-mentioned porous membrane.
[Claim 6] The manufacture approach of the proton conductivity film using the monofunctional nature monomer which has neither a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical with the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, a phosphonic acid radical, or the phosphinic acid radical was carried out in the approach according to claim 5.
[Claim 7] With the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, a phosphonic acid radical, or the phosphinic acid radical was carried out in the approach according to claim 5 The manufacture approach of the proton conductivity film of making the polymer by which amine chlorination was carried out the part having the structure of cross linkage using the polyfunctional monomer which has neither the polyfunctional monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical nor a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical.
[Claim 8] While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical to a side chain in the hole of porous membrane, and has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain generate The manufacture approach of the proton conductivity film which is made to support this polymer in the hole of the above-mentioned porous membrane, and is further characterized by carrying out the amine chlorination of a part of phosphoric-acid radical of the above-mentioned side chain of this polymer, phosphonic acid radical, or phosphinic acid radical.
[Claim 9] The manufacture approach of the proton conductivity film using the monofunctional nature monomer which has neither a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical in an approach according to claim 8 with the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain.

[Claim 10] The manufacture approach of the proton conductivity film of making a polymer having the structure of cross linkage in an approach according to claim 8 using the polyfunctional monomer which has neither the polyfunctional monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical nor a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical with the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain.
[Claim 11] Claims 5-10 which are what porous membrane becomes from ultrahigh-molecular-weight polyolefin resin or a fluororesin are the manufacture approaches of the proton conductivity film a publication either.
[Claim 12] The phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, The polymerization of the monomer mixture containing the monofunctional nature monomer by which the amine chlorination of a phosphonic acid radical or the phosphinic acid radical was carried out is carried out in the hole of porous membrane. While making the polymer by which amine chlorination was carried out generate, a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical The manufacture approach of the proton conductivity film which is made to support this polymer in the hole of the above-mentioned porous membrane, obtains the proton conductivity film, and is subsequently characterized by blockading a part of opening [at least] of the remainder of the hole of this proton conductivity film.
[Claim 13] The manufacture approach of the proton conductivity film using the monofunctional nature monomer which has neither a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical with the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, a phosphonic acid radical, or the phosphinic acid radical was carried out in the approach according to claim 12.
[Claim 14] With the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, a phosphonic acid radical, or the phosphinic acid radical was carried out in the approach according to claim 12 The polyfunctional monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical, and/or a phosphoric-acid radical, The manufacture approach of a proton conductivity film of making the polymer by which amine chlorination was carried out the part having the structure of cross linkage using the polyfunctional monomer which has neither a phosphonic acid radical nor a phosphinic acid radical.
[Claim 15] While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical to a side chain in the hole of porous membrane, and has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain generate This polymer is made to support in the hole of the above-mentioned porous membrane, further, the amine chlorination of a part of phosphoric-acid radical of the above-mentioned side chain of this polymer, phosphonic acid radical, or phosphinic acid radical is carried out, and the proton conductivity film is obtained. Subsequently The manufacture approach of the proton conductivity film characterized by blockading a part of opening [at least] of the remainder of the hole of this proton conductivity film.
[Claim 16] The manufacture approach of the proton conductivity film using the monofunctional nature monomer which has neither a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical in an approach according to claim 15 with the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain.
[Claim 17] The manufacture approach of a proton conductivity film of making a polymer having the structure of cross linkage in an approach according to claim 15 using the polyfunctional monomer which has neither the polyfunctional monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical nor a phosphoric-acid radical nor a phosphonic acid radical nor a phosphinic acid radical with the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain.
[Claim 18] The manufacture approach of a proton conductivity film given in either of claims 12-17 which are what porous membrane becomes from ultrahigh-molecular-weight polyolefin resin or a fluororesin.
[Claim 19] The fuel cell which comes to use the proton conductivity film of a publication for either of claims 1-3 as proton exchange film.
[Claim 20] The fuel cell which comes to use a proton conductivity film according to claim 4 as proton

· exchange film.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the proton conductivity film which has proton conductivity, the proton conductivity films obtained from this, those manufacture approaches, and the fuel cell which comes to use these proton conductivity film or a film as proton exchange film further.
[0002]
[Description of the Prior Art] Conventionally, although the proton conductivity film is used for the application of ion exchange membrane, a humidity sensor, etc., it attracts attention in recent years also in the application as a solid-electrolyte membrane in a polymer electrolyte fuel cell. For example, these fluororesin system proton conductivity film with which the sulfonic group content fluororesin film which makes Nafion (trademark) of Du Pont representation is conventionally known although the use as a solid electrolyte in an electric vehicle or the fuel cell for dispersed-type power sources is considered has the fault that a price is very high. In order to attain utilization for the proton conductivity film in new applications, such as a fuel cell, it is high in proton conductivity and it is indispensable to make a price low moreover.
[0003] Then, conventionally, the porous membrane which has a hole is made to contain an electrolyte polymer, and the method of obtaining the proton conductivity film is proposed variously. For example, after infiltrating into JP,9-194609,A the solution of the hydrophobic polymer same in the hole of the porous membrane which consists of hydrophobic resin, such as a fluororesin, polyethylene resin, and polypropylene resin, making it dry and making porous membrane support the above-mentioned polymer, ion exchange groups, such as a sulfonic group, a protonation amino group, and a carboxyl group, are introduced into this polymer, and the method of manufacturing ion exchange membrane is proposed in this way. However, according to such an approach, it is difficult to distribute an ion exchange group in porous membrane at homogeneity, as a result it is not enough. [of proton conductivity]
[0004] Then, the polymer which has a phosphoric ester radical as an ion exchange group recently, namely, the thing for which the polymer led to a side chain from the methacrylic-acid derivative which has a phosphoric ester radical is used as proton exchange film for polymer electrolyte fuel cells -- "the collection of the Society of Polymer Science, Japan drafts" -- the 414th page (1999) of the 3 volume [48th] No. "the collection of the Society of Polymer Science, Japan drafts" -- the 48th volume the 2393rd page (1999) and "the collection of the Society of Polymer Science, Japan drafts" of No. 10 -- it is proposed by the 751st page (2000) of the 4 volume [49th] No. etc.
[0005] The polymer which is led to a side chain from the methacrylic-acid derivative which has a phosphoric ester radical according to these reference has the large proton degree of dissociation of the above-mentioned phosphoric ester radical, and since strong acidity is shown, it has high proton conductivity, and though a principal chain is a hydrocarbon, while having thermal resistance, moreover, it has the property of hardly dissolving in water. Thus, it is concluded that it is because a network strong between polymer chains is formed of the hydrogen bond which a phosphoric ester radical forms between each that the polymer which it has in a side chain by making a phosphoric ester radical into a substituent is water-insoluble nature.
[0006] However, the above-mentioned polymer itself led to a side chain from the methacrylic-acid derivative which has a phosphoric ester radical has a low mechanical strength, and since it is weak, it is difficult [it] to use as proton exchange film for fuel cells. Moreover, it often gels at the time of the manufacture, and, in addition, there are many problems in respect of manufacture and a moldability for utilization -- the above-mentioned polymer is deficient in the obtained polymer to solubility.

[0007] Generally, in order to give proton conductivity to porous membrane, it is required in the film to have a proton generation source or a transportation site, and the sulfonic group which made reference previously is the example of representation of such a proton generation source or a transportation site. However, the polymers which have a sulfonic group are polystyrene sulfonate, a polyvinyl sulfonic acid, etc. typically, and these are all water solubility. Therefore, as proton exchange film of the fuel cell which carries out steam humidification and uses hydrogen gas and oxygen gas, if these polymers remain as they are, they are difficult to use. That is, in order to use as proton exchange film of a fuel cell, it is required for a polymer to perform a certain water-insoluble nature-ized processing.
[0008] In order to carry out water insolubilization of the water-soluble polymer, it is necessary to perform a monomer and copolymerization which give a water-insoluble nature polymer with the monomer which carries out bridge formation processing or has a sulfonic group, and to consider as a copolymer.
[0009] However, even if it is avoidable to dissolve in water completely by performing bridge formation processing to a water-soluble polymer, it is not avoided that a polymer swells when water is contacted. In this way, since the water insolubilization by bridge formation of a water-soluble polymer brings about the fall of the mechanical strength of a polymer in exchange for it, it is difficult to use the polymer which carried out water insolubilization of the water-soluble polymer as proton exchange film for fuel cells such.
[0010] On the other hand, since the proton conductivity which does not obtain a low kink colander relatively, then is originally searched for as proton exchange film by copolymerization with the monomer which gives a water-insoluble nature polymer in the rate of the sulfonic group content monomer in the monomer with which a polymerization is presented in order to obtain a water-insoluble nature polymer is spoiled, the polymer which has high proton conductivity cannot be obtained.
[0011]
[Problem(s) to be Solved by the Invention] This invention is made in order to solve the problem in the proton conductivity film or a film mentioned above, and it aims at offering the proton conductivity film or films which have endurance and a mechanical strength, those manufacture approaches, and the fuel cell which comes to use them as proton exchange film further.
[0012]
[Means for Solving the Problem] According to this invention, the proton conductivity film with which a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical is characterized by making it come to support the polymer by which amine chlorination was carried out in the hole of porous membrane is offered.
[0013] Furthermore, according to this invention, the proton conductivity film with which it comes to blockade a part of opening [at least] of the remainder of the hole of the above-mentioned proton conductivity film is offered.
[0014] Moreover, the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain according to this invention, and a side chain, While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer by which the amine chlorination of a phosphonic acid radical or the phosphinic acid radical was carried out in the hole of porous membrane and by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out generate The manufacture approach of the proton conductivity film characterized by making this polymer support in the hole of the above-mentioned porous membrane is offered.
[0015] Furthermore, according to this invention, the polymerization of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical is carried out to a side chain in the hole of porous membrane. While making a side chain generate the polymer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical This polymer is made to support in the hole of the above-mentioned porous membrane, and the manufacture approach of the proton conductivity film further characterized by carrying out the amine chlorination of a part of phosphoric-acid radical of the above-mentioned side chain of this polymer, phosphonic acid radical, or phosphinic acid radical is offered.
[0016] Moreover, the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain according to this invention, and a side chain, The polymerization of the monomer mixture containing the monofunctional nature monomer by which the amine chlorination of a phosphonic acid radical or the phosphinic acid radical was carried out is carried out in the hole of porous membrane. While making the polymer by which amine chlorination was carried out generate, a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical This polymer is made to support in the hole of the above-mentioned

porous membrane, the proton conductivity film is obtained, and the manufacture approach of the proton conductivity film subsequently characterized by blockading a part of opening [at least] of the remainder of the hole of this proton conductivity film is offered.

[0017] Furthermore, according to this invention, the polymerization of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical is carried out to a side chain in the hole of porous membrane. While making a side chain generate the polymer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical This polymer is made to support in the hole of the above-mentioned porous membrane, further, the amine chlorination of a part of phosphoric-acid radical of the above-mentioned side chain of this polymer, phosphonic acid radical, or phosphinic acid radical is carried out, and the proton conductivity film is obtained. Subsequently The manufacture approach of the proton conductivity film characterized by blockading a part of opening [at least] of the remainder of the hole of this proton conductivity film is offered.

[0018] According to this invention besides the above, the fuel cell which comes to use the above-mentioned proton conductivity film or a proton conductivity film as proton exchange film is offered.

[0019]

[Embodiment of the Invention] The proton conductivity film by this invention makes it come to support the polymer by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out in the hole of porous membrane.

[0020] In this invention, the polymer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain is hereafter called "P-polymer", and a part of phosphoric-acid radical of the above-mentioned side chain, phosphonic acid radical, or phosphinic acid radical calls the polymer by which amine chlorination was carried out "the partial amine salt of P-polymer."

[0021] According to this invention, such proton conductivity film The phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain preferably, and a side chain, While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer by which the amine chlorination of a phosphonic acid radical or the phosphinic acid radical was carried out in the hole of porous membrane and by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out generate It can obtain by making this polymer support in the hole of the above-mentioned porous membrane.

[0022] In this invention, the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain is hereafter called "P-monomer", and the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical, phosphonic acid radical, or phosphinic acid radical of a side chain was carried out is called "P-salt monomer." Moreover, the above-mentioned phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical is called "P-acid radical."

[0023] Moreover, the mixture of P-salt monomer and P-monomer is called "partial amine salt of P-monomer."

[0024] What consists of various resin can be used especially for the porous membrane used as a base material in the proton conductivity film by this invention, without being limited. As such resin, for example, fluororesins, such as polytetrafluoroethylene, Polyester resin, such as various polyamide resin besides 6 and 6-nylon, and polyethylene terephthalate, Polyether resin, such as dimethyl phenylene oxide and a polyether ether ketone, Alicyclic partial saturation ******, such as alpha olefins, such as ethylene and a propylene, and norbornene, Polymers, such as conjugated dienes, such as a butadiene and an isoprene, (**) for example, polyethylene resin and polypropylene resin -- moreover, aliphatic hydrocarbon resin, such as elastomers, such as ethylene-propylene rubber, butadiene rubber, polyisoprene rubber, isobutylene isoprene rubber, and polynorbornene rubber, and those water garnishes, can be mentioned. These resin is independent, or may use two or more sorts together, and may form the above-mentioned porous membrane.

[0025] They are polyolefin resin, especially weight average molecular weight 5.0x105 also in the porous membrane which consists of the above-mentioned various resin according to this invention. It is 1.0x106 preferably above. From the place the porous membrane which consists of the above amount polyethylene resin of giant molecules excels [place] in reinforcement or thermal resistance, it is used preferably. Moreover, the porous membrane which consists of fluororesins, such as polytetrafluoroethylene and polyvinylidene fluoride, is also preferably used in this invention from the outstanding chemical resistance and thermal resistance.

[0026] According to this invention, hydrophilization of the base material porous membrane may be carried

out by the proper means known conventionally. Such porous membrane by which hydrophilization was carried out can be obtained by usi[illegible]r a raw material the polymer which ha[illegible]drophilic radicals, such as a sulfonic group, a phosphoric-aci[illegible]ical, a carboxyl group, an amino group, [illegible] amide group, and a hydroxyl group, and its blend, and producing a film. Moreover, after producing a polymer without such a hydrophilic radical to porous membrane, for example, sulfonation processing can be performed and it can obtain by the approach of making the porous membrane support a surfactant etc.

[0027] In this invention, base material porous membrane usually has the void content of 30 - 85% of range preferably 20 to 90%. When the void content of porous membrane is smaller than 20%, even if it makes the hole of such porous membrane support the partial amine salt of P-polymer, the film which has high proton conductivity cannot be obtained. However, when the void content of porous membrane is larger than 90%, the proton conductivity film which the hole of such porous membrane is made to support the partial amine salt of P-polymer, and is obtained does not have enough reinforcement, and difficulty follows it on handling or use for various applications.

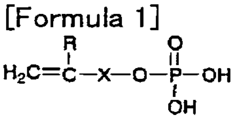
[0028] Moreover, although it is not especially limited if base material porous membrane can hold the partial amine salt of P-polymer in porous membrane, the range of the average aperture is 0.001-100 micrometers, and it is usually desirable that it is in the range of 0.005-10 micrometers. Similarly, although the thickness of porous membrane is not limited especially, either, it is 1mm or less and is usually the range of 5-500 micrometers preferably.

[0029] The proton conductivity film by this invention can be obtained by making the partial amine salt of this P-polymer support in the hole of the above-mentioned porous membrane while infiltrating the partial amine salt of P-monomer into porous membrane, carrying out a polymerization in the hole of this porous membrane preferably and making the partial amine salt of P-polymer generate.

[0030] It is a general formula (I) as an example with the monomer desirable according to this invention which has a phosphoric-acid radical among the above-mentioned P-monomers.

[0031]

[Formula 1]



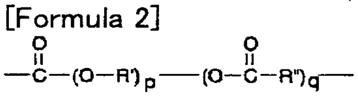
(I)

[0032] (— R shows a hydrogen atom or a methyl group among a formula, and X shows the divalent organic radical whose both ends of a radical are carbon atoms.) — the compound expressed can be mentioned.

[0033] Setting to this invention especially, the above-mentioned radical X is a general formula (A) preferably.

[0034]

[Formula 2]

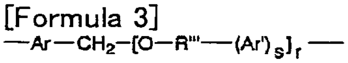


(A)

[0035] (— inside of formula, and R' — ethylene or a propylene radical — being shown — R″ — the carbon atomic numbers 1-10 — preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, p is the integer of 1-10, and q is 0, 1, or 2.) — the divalent radical expressed — or general formula (B)

[0036]

[Formula 3]

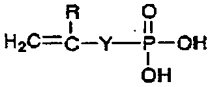


(B)

[0037] (— inside of formula, Ar, and Ar' — an independently divalent respectively aromatic hydrocarbon radical — desirable — a phenylene group — being shown — R' — preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, r is 0 or 1, and the carbon atomic numbers 1-10 and when r is 1, s of ″is 0 or 1.) — the divalent radical expressed is shown.

[0038] Therefore, as a desirable example of P-monomer expressed with the above-mentioned general formula (I), 2-methacryloiloxy-ethyl phosphate, methacryloyl tetrapod (oxyethylene) phosphate, methacryloyl PENTA (oxypropylene) phosphate, 4-styryl methoxy butyl phosphate, etc. can be mentioned, for example.

[0039] As a desirable example of the monomer which has a phosphonic acid radical, it is a general formula (II).
[0040]
[Formula 4]



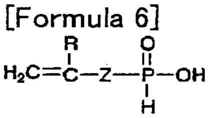
(II)

[0041] (— R shows a hydrogen atom or a methyl group among a formula, and Y shows the divalent organic radical whose both ends of a radical are carbon atoms.) -- the compound expressed can be mentioned.
[0042] Setting to this invention especially, the above-mentioned radical Y is a general formula (B) preferably.
[0043]
[Formula 5]

$$—Ar—CH_2-[O—R'''—(Ar')_s]_r—$$

(B)

[0044] (— inside of formula, Ar, and Ar' -- an independently divalent respectively aromatic hydrocarbon radical — desirable -- a phenylene group — being shown -- R' -- preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, r is 0 or 1, and the carbon atomic numbers 1-10 and when r is 1, s of ″is 0 or 1.) -- the divalent radical expressed is shown.
[0045] Therefore, as a desirable example of the monomer which has the phosphonic acid radical expressed with the above-mentioned general formula (II), compounds, such as 4-(2-styryl methoxy ethyl) phenylphosphonic acid, 4-(styryl methoxy) butyl phosphonic acid, and styryl methylphosphonic acid, can be mentioned, for example.
[0046] Moreover, as a desirable example of the monomer which has a phosphinic acid radical, it is a general formula (III) [0047].
[Formula 6]



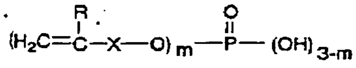
(III)

[0048] (-- R shows a hydrogen atom or a methyl group among a formula, and Z shows the divalent organic radical whose both ends of a radical are carbon atoms.) -- the compound expressed can be mentioned.
[0049] Setting to this invention especially, the above-mentioned radical Z is a general formula (B) preferably.
[0050]
[Formula 7]

$$—Ar—CH_2-[O—R'''—(Ar')_s]_r—$$

(B)

[0051] (— inside of formula, Ar, and Ar' -- an independently divalent respectively aromatic hydrocarbon radical -- desirable -- a phenylene group -- being shown -- R' -- preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, r is 0 or 1, and the carbon atomic numbers 1-10 and when r is 1, s of ″is 0 or 1.) -- the divalent radical expressed is shown.
[0052] Therefore, as an example of the monomer which has the phosphinic acid radical expressed with the above-mentioned general formula (III), compounds, such as 4-(2-styryl methoxy ethyl) phenyl phosphinic acid, 4-(styryl methoxy) butyl phosphinic acid, and styryl methyl phosphinic acid, can be mentioned, for example.
[0053] According to this invention, in manufacture of the partial amine salt of P-polymer, the polyfunctional monomer (it may be hereafter called a polyfunctional P-monomer) which has P-acid radical with the partial amine salt of P-monomer can be used.
[0054] As a desirable example of such a polyfunctional P-monomer, it is a general formula (IV).
[0055]
[Formula 8]



(IV)

[0056] (— R and X are the same as the above among a formula, and m is 2 or 3.) — the phosphoric-acid diester or triester expressed can be mentioned.
[0057] Especially in this invention, that whose radical X is a radical expressed with said general formula (A) among such polyfunctional P-monomers is desirable.
[0058] Therefore, phosphoric-acid diester, such as for example, screw (methacryloiloxy-ethyl) phosphate, screw {5-(methacryloyloxy ethyloxy carbonyl) pentyl} phosphate, etc., can be mentioned as an example of such a polyfunctional P-monomer.
[0059] When the partial amine salt of P-monomer contains such a polyfunctional P-monomer, the rate of this polyfunctional P-monomer is less than [50 mol %], and is less than [45 mol %] preferably.
[0060] Thus, by using a polyfunctional P-monomer with the partial amine salt of P-monomer, by the crosslinking reaction of the above-mentioned polyfunctional P-monomer, the partial amine salt of P-polymer obtained has the three-dimensional structure, i.e., the structure of cross linkage, and can improve further physical properties, such as the water resisting property of the partial amine salt of P-polymer, and solvent resistance, in this way.
[0061] Moreover, according to this invention, the polyfunctional monomer (it may be hereafter called a polyfunctional un-P-monomer) which has neither of P-acid radical with the partial amine salt of P-monomer can be used. Thus, when P-monomer partial amine salt contains a polyfunctional un-P-monomer, the rate of this polyfunctional un-P-monomer is less than [50 mol %], and is less than [45 mol %] preferably.
[0062] Thus, the partial amine salt of P-polymer obtained can also adjust various physical properties, for example, glass transition temperature, extent of a hydrophilic property, flexibility, a mechanical strength, etc. by using a polyfunctional un-P-monomer with the partial amine salt of P-monomer.
[0063] However, in the proton conductivity film by this invention, it is not limited above and, as for the means for giving the structure of cross linkage to the partial amine salt of P-polymer, the exposure of the reaction between functional groups, bridge formation according [for example,] to a peroxide, an electron ray, etc., an operation of ozone, etc. can use the proper means known from before.
[0064] Furthermore, according to this invention, the partial amine salt and copolymer of P-monomer may be made to form with the partial amine salt of P-monomer using the monofunctional nature monomer (for it to be hereafter called a single functionality un-P-monomer) which has neither of P-acid radical.
[0065] As such a single functionality un-P-monomer, acrylamides, such as acrylic monomers, such as vinyl ether, such as vinyl monomers, such as styrene, a vinyl sulfonic acid, and styrene sulfonic-acid sodium, and ethyl vinyl ether, butyl acrylate, methoxy ethyl acrylate, 2-ethylhexyl methacrylate, and an acrylic acid, N,N-dimethylaminopropyl acrylamide, and 2-acrylamido-2-methyl propane sulfonic acid, can be mentioned, for example.
[0066] In this invention, when using a single functionality un-P-monomer with the partial amine salt (a polyfunctional P-monomer is included.) of P-monomer, although the rate of the single functionality un-P-monomer is based also on the void content of the base material porous membrane to be used, the range of it is not more than 90 mol % to the partial amine salt (a polyfunctional P-monomer is included.) of P-monomer, and the range of it is usually not more than 80 mol % preferably. To the partial amine salt (a polyfunctional P-monomer is included.) of P-monomer, the rate of a single functionality un-P-monomer cannot obtain the high proton conductivity film, when [than 90 mol %] more.
[0067] In order to carry out the amine chlorination of the P-acid radical of P-monomer (i.e., for obtaining P-monomer by which the amine chlorination of the P-acid radical was carried out), an amine is made to act on P-monomer in this invention.
[0068] Here, although especially the above-mentioned amine is not limited here, it can mention ampholite, such as amino acid, such as alkanolamines, such as fatty amines, such as aromatic amines, such as heterocyclic amine, such as a pyridine, a quinoline, an acridine, an imidazole, a pyrazole, a piperidine, and a piperazine, the derivative and an aniline, a toluidine, benzylamine, a diphenylamine, and a naphthylamine, the derivative and n butylamine, and n-hexylamine, the derivative and monoethanolamine, and diethanolamine, a glycine, and glutamic acid, and a betaine, etc., for example
[0069] According to this invention, the partial amine salt of said P-monomer can make an amine able to act on P-monomer, and can be obtained as mixture with P-monomer which carried out amine chlorination with P-monomer which has not carried out amine chlorination so that the ratio R of P-acid radical which the

amino group / P-monomer of an amine have may be preferably set to 0< R<1. As for especially the ratio R of P-acid radical which the amino group / P-monomer of an amine have in the partial amine salt of P-monomer according to this invention, it is desirable that it is the range of 0.1<=R<=0.9.

[0070] However, according to this invention, the amine chlorination of all the P-monomers is carried out, this amine chlorination P-monomer and P-monomer which has not carried out amine chlorination can be mixed, and this can also be made into the partial amine salt of P-monomer. therefore, P-monomer which has not carried out amine chlorination in this case with P-monomer which carried out amine chlorination -- setting -- each P-monomer -- being the same -- you may differ.

[0071] According to this invention, in this way, the proton conductivity film makes base material porous membrane support preferably the partial amine salt of P-monomer, P-monomers, such as a polyfunctional P-monomer, a polyfunctional un-P-monomer, and a single functionality un-P-monomer, and P-salt monomer mentioned above if needed, and the monomer which has copolymerization nature, and thermal polymerization, photopolymerization, etc. should just carry out the polymerization of the above-mentioned monomer by the proper approach learned from before. However, as a polymerization method, a photopolymerization method is simple and those with insurance and a deer can also obtain the partial amine salt of P-polymer especially in a short time. Moreover, after performing photopolymerization, in order to carry out the polymerization of the residual monomer if needed, photopolymerization and thermal polymerization may be further performed more at an elevated temperature.

[0072] What is known conventionally should just be suitably used for the above-mentioned photopolymerization initiator. For example, the 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl) butanone -1 (Ciba-Geigy IRUGA cure 369), the 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino propanone -1 (Ciba-Geigy IRUGA cure 907), 1-hydroxy cyclohexyl phenyl ketone (Ciba-Geigy IRUGA cure 184), benzyl dimethyl ketal (Ciba-Geigy IRUGA cure 651), etc. can be used. Even if it uses light with a wavelength of 300nm or more, especially the thing in which a polymerization is possible is desirable. Such a photopolymerization initiator is usually added about 0.01 to 5% of the weight to the whole monomer containing the partial amine salt of P-monomer.

[0073] What is necessary is to immerse porous membrane in this mixture, and just to apply this mixture to base material porous membrane, for example, in order to make the partial amine salt of P-monomer, and the mixture which contains a copolymerization nature monomer, a photopolymerization initiator, etc. of said others if needed support in the hole of porous membrane.

[0074] Thus, it makes it face that porous membrane supports the mixture containing the partial amine salt of P-monomer, or it, and the viscosity of the mixture containing this P-monomer partial amine salt and it may be adjusted suitably. namely, a polymer proper in carrying out precuring of a part of partial amine salt of P-monomer, in order to raise viscosity -- small quantity -- you may make it add and dissolve On the contrary, a suitable solvent may be added and diluted in order to lower viscosity.

[0075] Thus, after making the mixture which contains the partial amine salt of P-monomer, and this in porous membrane support, pinch porous membrane with the mold releasing film made of polyester resin, and this exchange film is intercepted from oxygen (therefore, air). The proton conductivity film which makes the copolymerization nature monomer of the partial amine salt of P-monomer or others come to support the partial amine salt of P-polymer in the hole of porous membrane Mitsuteru putting and by carrying out photopolymerization using a high-pressure mercury lamp etc. can be obtained.

[0076] An optical exposure required for the above-mentioned photopolymerization is usually 0.1 - 5 J/cm2, although it changes with systems. Extent is enough. Photopolymerization is usually performed near a room temperature, in order to make high molecular weight of the partial amine salt of P-polymer obtained, but in order to raise conversion, it may perform photopolymerization at higher temperature. Moreover, it is low temperature at first and, subsequently you may photopolymerize at an elevated temperature.

[0077] Moreover, as an option, the proton conductivity film by this invention carries out the polymerization of the P-monomer to having mentioned above in the hole of porous membrane similarly, makes P-polymer generate, can make an amine able to act and, subsequently to this P-polymer, can be obtained also by amine-izing a part of that P-acid radical. According to this invention, an amine is made to act on P-polymer and an amine is made to act on P-polymer so that the ratio R of P-acid radical which the amino group / P-polymer of an amine have in this case may be set to 0< R<1, and the ratio R of P-acid radical which the amino group / P-polymer of an amine have may be preferably set to 0.1<=R<=0.9.

[0078] Thus, also when carrying out the polymerization of the P-monomer in the hole of porous membrane and making P-polymer generate, a polyfunctional P-monomer and a polyfunctional un-P-monomer can be used if needed, and P-polymer which has the structure of cross linkage can be made to be able to construct a bridge like the case where the polymerization of the partial amine salt of P-monomer is carried

out, and a copolymer with that can be made to generate using a monofunctional nature P-monomer.

[0079] According to this invention, [illegible] partial amine salt of P-monomer or P[illegible]omer, and the need are accepted. In case monomer mixtur[illegible]h the monomer of said others which h[illegible] copolymerization nature in these is infiltrated into porous membrane, when the ratio (filling factor) with which the above-mentioned monomer mixture fills up the hole of porous membrane is low The proton conductivity porous membrane in which base material porous membrane has the vesicular structure which has permeability, and after the polymerization of the above-mentioned monomer has permeability (carrying out the amine chlorination of the P-acid radical of generated P-polymer in being required) in this way can be obtained. On the other hand, when the above-mentioned filling factor is high, after the polymerization of the above-mentioned monomer, the hole is blockaded substantially and base material porous membrane can obtain the proton conductivity nonporous film without permeability (carrying out the amine chlorination of the P-acid radical of generated P-polymer, in being required). As a temporary standard, if the filling factor of a monomer is 80% or more, the proton conductivity nonporous film without the permeability which comes to blockade the hole of base material porous membrane substantially can be obtained.

[0080] In this invention, it the monomer mixture with the partial amine salt of P-monomer, P-monomer, and the monomer of the above which has copolymerization nature in these, and others is not only filled up with the hole of base material porous membrane, but may cover a part of one [at least] front face [at least] of base material porous membrane. In this case, the filling factor of the above-mentioned monomer mixture exceeds 100%. Thus, if base material porous membrane is made to support monomer mixture with the filling factor exceeding 100% and an optical exposure is carried out at this, it porous membrane is not only filled up with the polymer which the hole generates, but can obtain the proton conductivity film by which a part of one [at least (carrying out the amine chlorination of the P-acid radical of generated P-polymer, in being required)] front face [at least] was covered by the polymer.

[0081] Furthermore, the opening of the remainder of the hole which the proton conductivity film obtained by doing in this way has according to this invention, The opening which remains on the proton conductivity film obtained by doing in this way is heated and shrunk. Heating, carrying out melting, etc. suitably namely, with a means A part of above-mentioned opening [at least] which remains on the proton conductivity film is blockaded, and it can consider as a proton conductivity film, and especially, preferably, all the openings that remain on the proton conductivity film are blockaded, and a proton conductivity nonporous film without permeability can be obtained. Moreover, a part of opening which remains on the proton conductivity film is blockaded if needed, and a proton conductivity perforated film with permeability can be obtained.

[0082] Thus, the proton conductivity film and proton conductivity film of P-polymer which make it come to support a partial amine salt in the hole of base material porous membrane have high proton conductivity. The film and film which have high proton conductivity can be obtained, so that according to this invention the filling factor of the monomer mixture containing the partial amine salt of P-monomer to porous membrane or this is made high and the filling factor of the partial amine salt of P-polymer to the hole which porous membrane has is made high.

[0083] According to this invention, the proton conductivity film of nonporous structure can be obtained the proton conductivity film which has a vesicular structure and has permeability in this way, the proton conductivity film which can obtain the proton conductivity film of nonporous structure, and has a vesicular structure on the contrary, and has permeability, and reversely. For example, permselectivity charged membrane etc. can use preferably the proton conductivity film which has a vesicular structure and has permeability, and a film for the application which harnessed the opening.

[0084] However, the proton conductivity film and film which have a vesicular structure and have permeability have problems, like cross leak of gas tends to take place, if it uses as a separator for fuel cells. Therefore, it is desirable to use the proton conductivity nonporous film which comes to blockade all the openings that remain on the proton conductivity film with heating and proper means, such as to carry out melting, as the proton conductivity nonporous film which filled up the hole of porous membrane with the partial amine salt of P-polymer altogether substantially as mentioned above was used for such an application and proton conductivity porous membrane was mentioned above.

[0085] The proton conductivity film and proton conductivity film by this invention The proton conductivity polymer which consists of a partial amine salt of P-polymer is compound-ized to porous membrane. Preferably While infiltrating the partial amine salt of P-monomer into porous membrane, carrying out a polymerization in the hole of this porous membrane and making the partial amine salt of P-polymer generate The partial amine salt of this P-polymer is made to support in the hole of the above-mentioned porous membrane, and porous membrane and the partial amine salt of P-polymer are unified.

[0086] Therefore, according to this invention, it originates in compound-ization with base material porous membrane and a proton conductivity polymer, and the proton conductivity film or film which is various points and was excellent can be obtained. For example, in addition to the high proton conductivity originating in the partial amine salt of P-polymer, the proton conductivity film or film which has a high mechanical strength and the outstanding handling nature can be obtained by using the tough porous membrane which consists of ultra high molecular weight polyethylene etc. as a base material.
[0087] By making the partial amine salt of P-monomer support in the hole of porous membrane, carrying out a polymerization according to this invention, and uniting the partial amine salt of P-polymer with base material porous membrane especially The polymer chain of the partial amine salt of P-polymer can be twined around the mesh of porous membrane at altitude. Further If copolymerization of a polyfunctional P-monomer or the polyfunctional un-P-monomer is carried out with the partial amine salt of P-monomer Physical association arises by the polymer network as for which the partial amine salt of P-polymer which constructed the bridge, and the polymer chain which constitutes porous membrane carried out mutual penetration, and the proton conductivity film and film which strengthened the adhesion of a proton conductivity polymer and porous membrane further can be obtained in this way.
[0088]
[Example] Although an example is given to below and this invention is explained to it, this invention is not limited at all by these examples. Moreover, the property of the porous membrane used for below and the property of the obtained proton conductivity film or a film were evaluated as follows.
[0089] (Thickness of the film or a film) It measured by 1/10000 thickness gage.
(Void content of porous membrane) It computed by the bottom formula from weight [of per an unit area S (cm2)] W (g) of porous membrane, average thickness t (micrometer), and a consistency d (g/cm3).
[0090] Void content (%) = (1-(104 and W/(S-t-d)) x100[0091]) After leaving it for 4 hours under the environment which adjusted the proton conductivity film or a film to the temperature of 25 degrees C, and 50% of relative humidity, (Proton conductivity) Hewlett Packard LCR meter HP4284A is used. The sample of 1cm angle of given thickness Mino was inserted between platinum electrodes, it measured by the complex impedance method under conditions of the temperature of 25 degrees C, and 50% of relative humidity, and proton conductivity was computed using the resistance of the real part when extrapolating to the resistance zero of imaginary part.
[0092] (Rate of volume filling of the partial amine salt of P-polymer to the hole of base material porous membrane) It computed by the bottom formula from weight [of the volume V of base material porous membrane (cm3), void content / of base material porous membrane / phi, and the partial amine salt of (%) and P-polymer] M (g), and the consistency d of the partial amine salt of P-polymer (g/cm3).
[0093] Filling factor (%) =104 and M/(V-phi-d)
[0094] (Tensile strength) About the test piece (based on the No. 1 form test piece in JIS K 7113 and the tension test approach of plastics) pierced in the dumbbell mold, it measured using the tension tester (autograph AGS[by Shimadzu Corp.]-50D).
[0095] An example 1 70 % of the weight (light ester P-1 made from Kyoeisha Chemistry M) of P-monomers which consist of 2-methacryloiloxy-ethyl phosphate / screw (methacryloiloxy-ethyl) diphosphate (65 / 35 mole ratios) (Preparation of the partial amine salt of P-monomer) Stirring in the monomer mixture 100 weight section which consists of 30 % of the weight of methoxy ethyl acrylate The diethanolamine of the calculated requirements was added gradually beforehand and the monomer mixture which consists of the partial amine salt and methoxy ethyl acrylate of P-monomer of a phosphoric-acid radical of ratio R=1/2 was obtained. [of diethanolamine] [of the amino group / P-monomer]
[0096] (Manufacture of the proton conductivity film) The benzyl dimethyl ketal (Ciba-Geigy IRUGA cure 651) 0.25 weight section and the 1-hydroxy cyclohexyl phenyl ketone (Ciba-Geigy IRUGA cure 184) 0.25 weight section were dissolved in the above-mentioned monomer mixture 100 weight section.
[0097] It is weight average molecular weight 1.0x106 as it is, without diluting this. It applied to both sides of the porous membrane T1 (micrometers [of thickness / 25],% [of void contents / 40], 0.10 micrometers of average apertures) which consists of ultra-high-molecular-weight-polyethylene resin, and was made to sink into the hole of porous membrane.
[0098] Thus, the processed porous membrane is pinched with the mold releasing film made of polyester resin. The optical irradiation equipment (UB 021-1 made from Eye Graphic B-13) equipped with the high-pressure mercury lamp after intercepting porous membrane from air is used, and it is energy 1.5 J/cm2 to the above-mentioned porous membrane. An optical exposure is carried out. While carrying out photopolymerization of the above-mentioned monomer mixture in the hole and making the copolymer of the partial amine salt of P-polymer, and methoxy ethyl acrylate generate, this was made to support in the

hole of the above-mentioned porous membrane, and the proton conductivity film F1 with a thickness of 40 micrometers was obtained. In this proton conductivity film, the hole of porous membrane is completely filled up with the copolymer of the partial amine salt of the above-mentioned P-polymer, and methoxy ethyl acrylate, and both the front faces of porous membrane were also covered with the layer of the above-mentioned copolymer.

[0099] The proton conductivity of the above-mentioned proton conductivity film F1 was 2.3x10-3 S/cm, and tensile strength was 75MPa(s).

[0100] (Fuel cell) It is a platinum catalyst 0.6mg/cm 2 The above-mentioned proton conductivity film F1 was inserted between two carbon paper which the front face was made to support with a rate, it joined using the hotpress, and the film-electrode zygote (MEA) was manufactured.

[0101] The fuel cell property of Above MEA was evaluated using the fuel cell evaluation equipment by TOYO Corp. The back-pressure valve was not extracted but the pressure was performed in ordinary pressure. Humidifier temperature was made into 70 degrees C the 80-degree-C and oxygen side the hydrogen side, and fuel cell cel temperature was made into 70 degrees C. When the current-electrical-potential-difference (I-V) curve was obtained by the Tafel method, the current-electrical-potential-difference (I-V) curve almost equivalent to the case where Nafion (trademark) 117 film is used for a result as proton exchange film as shown in drawing 1 was obtained. That is, the proton conductivity film by this invention has a fuel cell property equivalent to Nafion 117 film.

[0102] Stirring in the P-monomer 100 weight section which consists of the same 2-methacryloiloxy-ethyl phosphate as example 2 (preparation of the partial amine salt of P-monomer) example 1, and screw (methacryloiloxy-ethyl) diphosphate, the powder of the imidazole of the calculated requirements was added gradually beforehand, and it considered as the partial amine salt of P-monomer of ratio R=1/3 of the phosphoric-acid radical of the amino group / P-monomer of an imidazole.

[0103] (Manufacture of the proton conductivity film) The benzyl dimethyl ketal (it is the same as the above) 0.25 weight section and the 1-hydroxy cyclohexyl phenyl ketone (it is the same as the above) 0.25 weight section were dissolved in the partial amine salt 100 weight section of the above-mentioned P-monomer.

[0104] The porous membrane T1 which consists of the same ultra-high-molecular-weight-polyethylene resin as an example 1 is carried on the mold releasing film made of polyester resin, without diluting the partial amine salt of the above-mentioned P-monomer, as it is, it applied to the exposure front face of porous membrane, it drew through on it with the bar, the excessive monomer was removed on it from the front face of porous membrane, and the partial amine salt of the above-mentioned P-monomer was infiltrated into it only all over the hole of porous membrane.

[0105] Thus, the mold releasing film made of polyester resin is put also on the exposure front face of the processed porous membrane, porous membrane is intercepted from air, the same optical irradiation equipment as an example 1 is used, and it is energy 1.5 J/cm2. An optical exposure is carried out at porous membrane. While carrying out photopolymerization of the partial amine salt of the above-mentioned P-monomer in that hole and making the partial amine salt of P-polymer generate, the partial amine salt of this P-polymer was made to support in the above-mentioned hole, and the proton conductivity film F2 with a thickness of 25 micrometers was obtained. In this proton conductivity film, the hole of porous membrane was completely filled up with the polymer. The proton conductivity of this proton conductivity film F2 was 1.2x10-3 S/cm.

[0106] Stirring in the P-monomer 100 weight section which consists of the same 2-methacryloiloxy-ethyl phosphate as example 3 (preparation of the partial amine salt of P-monomer) example 1, and screw (methacryloiloxy-ethyl) diphosphate, the aniline of the calculated requirements was added gradually beforehand and it considered as the partial amine salt of P-monomer of ratio R=1/5 of the phosphoric-acid radical of the amino group / P-monomer of an aniline.

[0107] (Manufacture of the proton conductivity film) The benzyl dimethyl ketal (it is the same as the above) 0.25 weight section and the 1-hydroxy cyclohexyl phenyl ketone (it is the same as the above) 0.5 weight section were dissolved in the partial amine salt 100 weight section of the above-mentioned P-monomer, and this was diluted with the methanol so that the partial amine salt concentration of P-monomer might become 30 % of the weight. It diluted.

[0108] Porous membrane T2 (40 micrometers of thickness) which consists of ultra-high-molecular-weight-polyethylene resin of weight average molecular weight 2.4x106 44% of void contents and 0.15 micrometers of average apertures are carried on the mold releasing film made of polyester resin. The diluted solution of the partial amine salt mixture of the above-mentioned P-monomer is applied, it draws through with a bar, and an excessive monomer is removed from the front face of porous membrane, it was air-dry on the

exposure front face of this porous membrane, and the partial amine salt of the above-mentioned P-monomer was infiltrated into it only over the hole of porous membrane.
[0109] Thus, the mold releasing film made of polyester resin is put also on the exposure front face of the processed porous membrane, porous membrane is intercepted from air, the same optical irradiation equipment as an example 1 is used, and it is energy 1.5 J/cm2. An optical exposure is carried out at porous membrane. While carrying out photopolymerization of the above-mentioned monomer mixture in that hole and making the partial amine salt of P-polymer generate, the partial amine salt of this P-polymer was made to support in the above-mentioned hole, and the proton conductivity film F3 with a thickness of 40 micrometers was obtained. In this proton conductivity film, the hole of porous membrane was partially filled up with the partial amine salt of P-polymer. The proton conductivity of this proton conductivity film F3 was 8.5x10-5 S/cm.
[0110] In example of comparison 1 example 1, the monomer mixture containing the partial amine salt of the P-monomer same on the mold releasing film made of polyester resin as an example 1 was applied to the layer with a thickness of 40 micrometers, without using base material porous membrane.
[0111] The mold releasing film made of polyester resin is carried also on this spreading layer, the spreading layer of the partial amine salt of the above-mentioned monomer mixture is intercepted from air, the same optical irradiation equipment as an example 1 is used, and it is energy 1.5J/cm2. Carried out the optical exposure, the copolymer of the partial amine salt of P-polymer and methoxy ethyl acrylate was made to generate, and the proton conductivity film R1 with a thickness of 40 micrometers it is thin only from this copolymer was obtained. The proton electric conductivity of this proton conductivity film was 2.6x10-3 S/cm, and tensile strength was 9MPa.
[0112] After having carried out the ion exchange of the water solution (poly eggplant PS[by TOSOH CORP.]- 5) of example of comparison 2 sodium polystyrene sulfonate using strong acid nature cation exchange resin, changing sodium salt into the free acid and condensing this, it was made to dissolve in a methanol and the methanol solution of the polystyrene sulfonate of concentration was prepared 20%.
[0113] The porous membrane T2 which consists of the same ultra-high-molecular-weight-polyethylene resin as an example 3 was put on the mold releasing film made of polyester resin, the methanol solution of the above-mentioned polystyrene sulfonate is applied to the exposure front face, it was dried, and the proton conductivity film R2 with a thickness of 58 micrometers was obtained.
[0114] In this proton conductivity film, the hole of porous membrane is completely filled up with the above-mentioned polystyrene sulfonate, and the front face by the side of spreading of the above-mentioned polystyrene sulfonate of porous membrane was also covered with the layer of polystyrene sulfonate. The proton conductivity of this proton conductivity film R2 was 2.0x10-5 S/cm.
[0115] When gas conditioning of this proton conductivity film was again carried out to the temperature of 25 degrees C, and 50% of relative humidity after being immersed to this water as a result of eluting a part of polystyrene sulfonate underwater, when immersed in water for 24 hours, and proton conductivity was measured, it was 3.7x10-6 S/cm.
[0116]
[Effect of the Invention] As mentioned above, the proton conductivity film by this invention makes it come to support the partial amine salt of P-polymer by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out in the hole of porous membrane, and it not only has high proton conductivity, but it has high reinforcement, and the partial amine salt of the above-mentioned P-polymer is water-insoluble nature further.
[0117] While carrying out the polymerization of the partial amine salt of P-monomer in the hole of porous membrane and making the partial amine salt of P-polymer generate especially according to this invention, according to the proton conductivity film which makes it come to support the partial amine salt of this P-polymer in the hole of the above-mentioned porous membrane, the partial amine salt and porous membrane of P-polymer are unified, and, as for the partial amine salt of P-polymer, it has advanced adhesion to porous membrane. and the proton conductivity film by this invention can be markedly boiled compared with the proton conductivity film which consists of the conventional sulfonic group content fluororesin film, and can be obtained cheap.
[0118] In this way, the proton conductivity film by this invention can be suitably used as ion exchange membrane in a fuel cell, here, since it is cheap here, makes it able to reduce the cost of a fuel cell system sharply, and can speed up the utilization.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the proton conductivity film which has proton conductivity, the proton conductivity films obtained from this, those manufacture approaches, and the fuel cell which comes to use these proton conductivity film or a film as proton exchange film further.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Conventionally, although the proton conductivity film is used for the application of ion exchange membrane, a humidity sensor, etc., it attracts attention in recent years also in the application as a solid-electrolyte membrane in a polymer electrolyte fuel cell. For example, these fluororesin system proton conductivity film with which the sulfonic group content fluororesin film which makes Nafion (trademark) of Du Pont representation is conventionally known although the use as a solid electrolyte in an electric vehicle or the fuel cell for dispersed-type power sources is considered has the fault that a price is very high. In order to attain utilization for the proton conductivity film in new applications, such as a fuel cell, it is high in proton conductivity and it is indispensable to make a price low moreover.

[0003] Then, conventionally, the porous membrane which has a hole is made to contain an electrolyte polymer, and the method of obtaining the proton conductivity film is proposed variously. For example, after infiltrating into JP,9-194609,A the solution of the hydrophobic polymer same in the hole of the porous membrane which consists of hydrophobic resin, such as a fluororesin, polyethylene resin, and polypropylene resin, making it dry and making porous membrane support the above-mentioned polymer, ion exchange groups, such as a sulfonic group, a protonation amino group, and a carboxyl group, are introduced into this polymer, and the method of manufacturing ion exchange membrane is proposed in this way. However, according to such an approach, it is difficult to distribute an ion exchange group in porous membrane at homogeneity, as a result it is not enough. [of proton conductivity]

[0004] then, the thing for which the polymer which has a phosphoric ester radical as an ion exchange group, i.e., the polymer led to a side chain from the methacrylic-acid derivative which has a phosphoric ester radical, is used as proton exchange film for polymer electrolyte fuel cells recently -- "the collection of the Society of Polymer Science, Japan drafts" -- the 414th page (1999) of the 3 volume [48th] No., "the collection of the Society of Polymer Science, Japan drafts" -- the 48th volume the 2393rd page (1999) and "the collection of the Society of Polymer Science, Japan drafts" of No. 10 -- it is proposed by the 751st page (2000) of the 4 volume [49th] No. etc.

[0005] The polymer which is led to a side chain from the methacrylic-acid derivative which has a phosphoric ester radical according to these reference has the large proton degree of dissociation of the above-mentioned phosphoric ester radical, and since strong acidity is shown, it has high proton conductivity, and though a principal chain is a hydrocarbon, while having thermal resistance, moreover, it has the property of hardly dissolving in water. Thus, it is concluded that it is because a network strong between polymer chains is formed of the hydrogen bond which a phosphoric ester radical forms between each that the polymer which it has in a side chain by making a phosphoric ester radical into a substituent is water-insoluble nature.

[0006] However, the above-mentioned polymer itself led to a side chain from the methacrylic-acid derivative which has a phosphoric ester radical has a low mechanical strength, and since it is weak, it is difficult [it] to use as proton exchange film for fuel cells. Moreover, it often gels at the time of the manufacture, and, in addition, there are many problems in respect of manufacture and a moldability for utilization -- the above-mentioned polymer is deficient in the obtained polymer to solubility.

[0007] Generally, in order to give proton conductivity to porous membrane, it is required in the film to have a proton generation source or a transportation site, and the sulfonic group which made reference previously is the example of representation of such a proton generation source or a transportation site. However, the polymers which have a sulfonic group are polystyrene sulfonate, a polyvinyl sulfonic acid, etc. typically, and these are all water solubility. Therefore, as proton exchange film of the fuel cell which carries out steam humidification and uses hydrogen gas and oxygen gas, if these polymers remain as they are, they

are difficult to use. That is, in order to use as proton exchange film of a fuel cell, it is required for a polymer to perform a certain water-insoluble nature-ized processing.
[0008] In order to carry out water insolubilization of the water-soluble polymer, it is necessary to perform a monomer and copolymerization which give a water-insoluble nature polymer with the monomer which carries out bridge formation processing or has a sulfonic group, and to consider as a copolymer.
[0009] However, even if it is avoidable to dissolve in water completely by performing bridge formation processing to a water-soluble polymer, it is not avoided that a polymer swells when water is contacted. In this way, since the water insolubilization by bridge formation of a water-soluble polymer brings about the fall of the mechanical strength of a polymer in exchange for it, it is difficult to use the polymer which carried out water insolubilization of the water-soluble polymer as proton exchange film for fuel cells such.
[0010] On the other hand, since the proton conductivity which does not obtain a low kink colander relatively, then is originally searched for as proton exchange film by copolymerization with the monomer which gives a water-insoluble nature polymer in the rate of the sulfonic group content monomer in the monomer with which a polymerization is presented in order to obtain a water-insoluble nature polymer is spoiled, the polymer which has high proton conductivity cannot be obtained.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, the proton conductivity film by this invention makes it come to support the partial amine salt of P-polymer by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out in the hole of porous membrane, and it not only has high proton conductivity, but it has high reinforcement, and the partial amine salt of the above-mentioned P-polymer is water-insoluble nature further.
[0117] While carrying out the polymerization of the partial amine salt of P-monomer in the hole of porous membrane and making the partial amine salt of P-polymer generate especially according to this invention, according to the proton conductivity film which makes it come to support the partial amine salt of this P-polymer in the hole of the above-mentioned porous membrane, the partial amine salt and porous membrane of P-polymer are unified, and, as for the partial amine salt of P-polymer, it has advanced adhesion to porous membrane. and the proton conductivity film by this invention can be markedly boiled compared with the proton conductivity film which consists of the conventional sulfonic group content fluororesin film, and can be obtained cheap.
[0118] In this way, the proton conductivity film by this invention can be suitably used as ion exchange membrane in a fuel cell, here, since it is cheap here, makes it able to reduce the cost of a fuel cell system sharply, and can speed up the utilization.

[Translation done.]

* NOTICES *

TECHNICAL PROBLEM

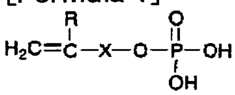
[Problem(s) to be Solved by the Invention] This invention is made in order to solve the problem in the proton conductivity film or a film mentioned above, and it aims at offering the proton conductivity film or films which have endurance and a mechanical strength, those manufacture approaches, and the fuel cell which comes to use them as proton exchange film further.

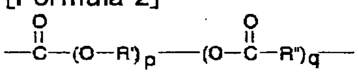
[Translation done.]

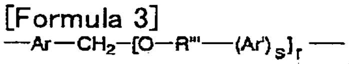
MEANS

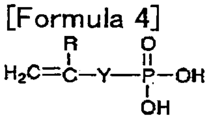
[Means for Solving the Problem] According to this invention, the proton conductivity film with which a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical is characterized by making it come to support the polymer by which amine chlorination was carried out in the hole of porous membrane is offered.
[0013] Furthermore, according to this invention, the proton conductivity film with which it comes to blockade a part of opening [at least] of the remainder of the hole of the above-mentioned proton conductivity film is offered.
[0014] moreover -- while making the polymer which is made to carry out the polymerization of the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, a phosphonic acid radical, or the phosphinic acid radical was carried out in the hole of porous membrane and by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out generate according to this invention The manufacture approach of the proton conductivity film characterized by making this polymer support in the hole of the above-mentioned porous membrane is offered.
[0015] While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical to a side chain in the hole of porous membrane, and furthermore has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain according to this invention generate This polymer is made to support in the hole of the above-mentioned porous membrane, and the manufacture approach of the proton conductivity film further characterized by carrying out the amine chlorination of a part of phosphoric-acid radical of the above-mentioned side chain of this polymer, phosphonic acid radical, or phosphinic acid radical is offered.
[0016] moreover -- while making the polymer which is made to carry out the polymerization of the monomer mixture containing the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain, and a side chain, a phosphonic acid radical, or the phosphinic acid radical was carried out in the hole of porous membrane and by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out generate according to this invention This polymer is made to support in the hole of the above-mentioned porous membrane, the proton conductivity film is obtained, and the manufacture approach of the proton conductivity film subsequently characterized by blockading a part of opening [at least] of the remainder of the hole of this proton conductivity film is offered.
[0017] While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical to a side chain in the hole of porous membrane, and furthermore has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain according to this invention generate This polymer is made to support in the hole of the above-mentioned porous membrane, further, the amine chlorination of a part of phosphoric-acid radical of the above-mentioned side chain of this polymer, phosphonic acid radical, or phosphinic acid radical is carried out, the proton conductivity film is obtained, and the manufacture approach of the proton conductivity film subsequently characterized by blockading a part of opening [at least] of the remainder of the hole of this proton conductivity film is offered.
[0018] According to this invention besides the above, the fuel cell which comes to use the above-

mentioned proton conductivity film or a proton conductivity film as proton exchange film is offered.
[0019]
[Embodiment of the Invention] The proton conductivity film by this invention makes it come to support the polymer by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out in the hole of porous membrane.
[0020] In this invention, the polymer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain is hereafter called "P-polymer", and a part of phosphoric-acid radical of the above-mentioned side chain, phosphonic acid radical, or phosphinic acid radical calls the polymer by which amine chlorination was carried out "the partial amine salt of P-polymer."
[0021] According to this invention, it is such proton conductivity film, The phosphoric-acid radical of the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain preferably, and a side chain, While making the polymer which is made to carry out the polymerization of the monofunctional nature monomer by which the amine chlorination of a phosphonic acid radical or the phosphinic acid radical was carried out in the hole of porous membrane and by which the amine chlorination of a part of phosphoric-acid radical of a side chain, phosphonic acid radical, or phosphinic acid radical was carried out generate It can obtain by making this polymer support in the hole of the above-mentioned porous membrane.
[0022] In this invention, the monofunctional nature monomer which has a phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical in a side chain is hereafter called "P-monomer", and the monofunctional nature monomer by which the amine chlorination of the phosphoric-acid radical, phosphonic acid radical, or phosphinic acid radical of a side chain was carried out is called "P-salt monomer." Moreover, the above-mentioned phosphoric-acid radical, a phosphonic acid radical, or a phosphinic acid radical is called "P-acid radical."
[0023] Moreover, the mixture of P-salt monomer and P-monomer is called "partial amine salt of P-monomer."
[0024] What consists of various resin can be used especially for the porous membrane used as a base material in the proton conductivity film by this invention, without being limited. As such resin For example, others [nylon / fluororesins /, such as polytetrafluoroethylene, /, 6, and 6-], Polyester resin, such as various polyamide resin and polyethylene terephthalate, Polyether resin, such as dimethyl phenylene oxide and a polyether ether ketone, Alicyclic partial saturation ******, such as alpha olefins, such as ethylene and a propylene, and norbornene, Polymers, such as conjugated dienes, such as a butadiene and an isoprene, (**) for example, polyethylene resin and polypropylene resin — moreover, aliphatic hydrocarbon resin, such as elastomers, such as ethylene-propylene rubber, butadiene rubber, polyisoprene rubber, isobutylene isoprene rubber, and polynorbornene rubber, and those water garnishes, can be mentioned. These resin is independent, or may use two or more sorts together, and may form the above-mentioned porous membrane.
[0025] They are polyolefin resin, especially weight average molecular weight 5.0x105 also in the porous membrane which consists of the above-mentioned various resin according to this invention. It is 1.0x106 preferably above. From the place the porous membrane which consists of the above amount polyethylene resin of giant molecules excels [place] in reinforcement or thermal resistance, it is used preferably. Moreover, the porous membrane which consists of fluororesins, such as polytetrafluoroethylene and polyvinylidene fluoride, is also preferably used in this invention from the outstanding chemical resistance and thermal resistance.
[0026] According to this invention, hydrophilization of the base material porous membrane may be carried out by the proper means known conventionally. Such porous membrane by which hydrophilization was carried out can be obtained by using for a raw material the polymer which has hydrophilic radicals, such as a sulfonic group, a phosphoric-acid radical, a carboxyl group, an amino group, an amide group, and a hydroxyl group, and its blend, and producing a film. Moreover, after producing a polymer without such a hydrophilic radical to porous membrane, for example, sulfonation processing can be performed and it can obtain by the approach of making the porous membrane support a surfactant etc.
[0027] In this invention, base material porous membrane usually has the void content of 30 - 85% of range preferably 20 to 90%. When the void content of porous membrane is smaller than 20%, even if it makes the hole of such porous membrane support the partial amine salt of P-polymer, the film which has high proton conductivity cannot be obtained. However, when the void content of porous membrane is larger than 90%, the proton conductivity film which the hole of such porous membrane is made to support the partial amine salt of P-polymer, and is obtained does not have enough reinforcement, and difficulty follows it on handling or use for various applications.

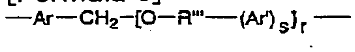
[0028] Moreover, although it is not especially limited if base material porous membrane can hold the partial amine salt of P-polymer in porous membrane, the range of the average aperture is 0.001-100 micrometers, and it is usually desirable that it is in the range of 0.005-10 micrometers. Similarly, although the thickness of porous membrane is not limited especially, either, it is 1mm or less and is usually the range of 5-500 micrometers preferably.
[0029] The proton conductivity film by this invention can be obtained by making the partial amine salt of this P-polymer support in the hole of the above-mentioned porous membrane while infiltrating the partial amine salt of P-monomer into porous membrane, carrying out a polymerization in the hole of this porous membrane preferably and making the partial amine salt of P-polymer generate.
[0030] It is a general formula (I) as an example with the monomer desirable according to this invention which has a phosphoric-acid radical among the above-mentioned P-monomers.
[0031]
[Formula 1]

(I)

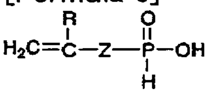
[0032] (-- R shows a hydrogen atom or a methyl group among a formula, and X shows the divalent organic radical whose both ends of a radical are carbon atoms.) -- the compound expressed can be mentioned.
[0033] Setting to this invention especially, the above-mentioned radical X is a general formula (A) preferably.
[0034]
[Formula 2]

(A)

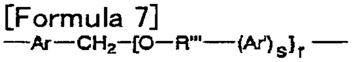
[0035] (-- inside of formula, and R' -- ethylene or a propylene radical -- being shown -- R″ -- the carbon atomic numbers 1-10 -- preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, p is the integer of 1-10, and q is 0, 1, or 2.) -- the divalent radical expressed -- or general formula (B)
[0036]
[Formula 3]

(B)

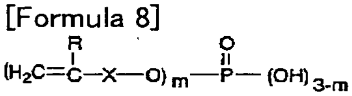
[0037] (-- inside of formula, Ar, and Ar' -- an independently divalent respectively aromatic hydrocarbon radical -- desirable -- a phenylene group -- being shown -- R' -- preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, r is 0 or 1, and the carbon atomic numbers 1-10 and when r is 1, s of ″is 0 or 1.) -- the divalent radical expressed is shown.
[0038] Therefore, as a desirable example of P-monomer expressed with the above-mentioned general formula (I), 2-methacryloiloxy-ethyl phosphate, methacryloyl tetrapod (oxyethylene) phosphate, methacryloyl PENTA (oxypropylene) phosphate, 4-styryl methoxy butyl phosphate, etc. can be mentioned, for example.
[0039] As a desirable example of the monomer which has a phosphonic acid radical, it is a general formula (II).
[0040]
[Formula 4]

(II)

[0041] (-- R shows a hydrogen atom or a methyl group among a formula, and Y shows the divalent organic radical whose both ends of a radical are carbon atoms.) -- the compound expressed can be mentioned.
[0042] Setting to this invention especially, the above-mentioned radical Y is a general formula (B) preferably.

[0043]
[Formula 5]

(B)

[0044] (— inside of formula, Ar, and Ar' — an independently divalent respectively aromatic hydrocarbon radical — desirable — a phenylene group — being shown — R' — preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, r is 0 or 1, and the carbon atomic numbers 1-10 and when r is 1, s of "is 0 or 1.) — the divalent radical expressed is shown.
[0045] Therefore, as a desirable example of the monomer which has the phosphonic acid radical expressed with the above-mentioned general formula (II), compounds, such as 4-(2-styryl methoxy ethyl) phenylphosphonic acid, 4-(styryl methoxy) butyl phosphonic acid, and styryl methylphosphonic acid, can be mentioned, for example.
[0046] Moreover, as a desirable example of the monomer which has a phosphinic acid radical, it is a general formula (III). [0047]
[Formula 6]

(III)

[0048] (— R shows a hydrogen atom or a methyl group among a formula, and Z shows the divalent organic radical whose both ends of a radical are carbon atoms.) — the compound expressed can be mentioned.
[0049] Setting to this invention especially, the above-mentioned radical Z is a general formula (B) preferably.
[0050]
[Formula 7]

(B)

[0051] (— inside of formula, Ar, and Ar' — an independently divalent respectively aromatic hydrocarbon radical — desirable — a phenylene group — being shown — R' — preferably, the shape of a straight chain and branched-chain alkylene group of 2-6 is shown, r is 0 or 1, and the carbon atomic numbers 1-10 and when r is 1, s of "is 0 or 1.) — the divalent radical expressed is shown.
[0052] Therefore, as an example of the monomer which has the phosphinic acid radical expressed with the above-mentioned general formula (III), compounds, such as 4-(2-styryl methoxy ethyl) phenyl phosphinic acid, 4-(styryl methoxy) butyl phosphinic acid, and styryl methyl phosphinic acid, can be mentioned, for example.
[0053] According to this invention, in manufacture of the partial amine salt of P-polymer, the polyfunctional monomer (it may be hereafter called a polyfunctional P-monomer) which has P-acid radical with the partial amine salt of P-monomer can be used.
[0054] As a desirable example of such a polyfunctional P-monomer, it is a general formula (IV).
[0055]
[Formula 8]

(IV)

[0056] (— R and X are the same as the above among a formula, and m is 2 or 3.) — the phosphoric-acid diester or triester expressed can be mentioned.
[0057] Especially in this invention, that whose radical X is a radical expressed with said general formula (A) among such polyfunctional P-monomers is desirable.
[0058] Therefore, phosphoric-acid diester, such as for example, screw (methacryloiloxy-ethyl) phosphate, screw {5-(methacryloyloxy ethyloxy carbonyl) pentyl} phosphate, etc., can be mentioned as an example of such a polyfunctional P-monomer.
[0059] When the partial amine salt of P-monomer contains such a polyfunctional P-monomer, the rate of this polyfunctional P-monomer is less than [50 mol %], and is less than [45 mol %] preferably.

[0060] Thus, by using a polyfunctional P-monomer with the partial amine salt of P-monomer, by the crosslinking reaction of the above-mentioned polyfunctional P-monomer, the partial amine salt of P-polymer obtained has the three-dimensional structure, i.e., the structure of cross linkage, and can improve further physical properties, such as the water resisting property of the partial amine salt of P-polymer, and solvent resistance, in this way.
[0061] Moreover, according to this invention, the polyfunctional monomer (it may be hereafter called a polyfunctional un-P-monomer) which has neither of P-acid radical with the partial amine salt of P-monomer can be used. Thus, when P-monomer partial amine salt contains a polyfunctional un-P-monomer, the rate of this polyfunctional un-P-monomer is less than [50 mol %], and is less than [45 mol %] preferably.
[0062] Thus, the partial amine salt of P-polymer obtained can also adjust various physical properties, for example, glass transition temperature, extent of a hydrophilic property, flexibility, a mechanical strength, etc. by using a polyfunctional un-P-monomer with the partial amine salt of P-monomer.
[0063] However, in the proton conductivity film by this invention, it is not limited above and, as for the means for giving the structure of cross linkage to the partial amine salt of P-polymer, the exposure of the reaction between functional groups, bridge formation according [for example,] to a peroxide, an electron ray, etc., an operation of ozone, etc. can use the proper means known from before.
[0064] Furthermore, according to this invention, the partial amine salt and copolymer of P-monomer may be made to form with the partial amine salt of P-monomer using the monofunctional nature monomer (for it to be hereafter called a single functionality un-P-monomer) which has neither of P-acid radical.
[0065] As such a single functionality un-P-monomer, acrylamides, such as acrylic monomers, such as vinyl ether, such as vinyl monomers, such as styrene, a vinyl sulfonic acid, and styrene sulfonic-acid sodium, and ethyl vinyl ether, butyl acrylate, methoxy ethyl acrylate, 2-ethylhexyl methacrylate, and an acrylic acid, N,N-dimethylaminopropyl acrylamide, and 2-acrylamido-2-methyl propane sulfonic acid, can be mentioned, for example.
[0066] In this invention, when using a single functionality un-P-monomer with the partial amine salt (a polyfunctional P-monomer is included.) of P-monomer, although the rate of the single functionality un-P-monomer is based also on the void content of the base material porous membrane to be used, the range of it is not more than 90 mol % to the partial amine salt (a polyfunctional P-monomer is included.) of P-monomer, and the range of it is usually not more than 80 mol % preferably. To the partial amine salt (a polyfunctional P-monomer is included.) of P-monomer, the rate of a single functionality un-P-monomer cannot obtain the high proton conductivity film, when [than 90 mol %] more.
[0067] In order to carry out the amine chlorination of the P-acid radical of P-monomer (i.e., for obtaining P-monomer by which the amine chlorination of the P-acid radical was carried out), an amine is made to act on P-monomer in this invention.
[0068] Here, although especially the above-mentioned amine is not limited here, it can mention ampholite, such as amino acid, such as alkanolamines, such as fatty amines, such as aromatic amines, such as heterocyclic amine, such as a pyridine, a quinoline, an acridine, an imidazole, a pyrazole, a piperidine, and a piperazine, the derivative and an aniline, a toluidine, benzylamine, a diphenylamine, and a naphthylamine, the derivative and n butylamine, and n-hexylamine, the derivative and monoethanolamine, and diethanolamine, a glycine, and glutamic acid, and a betaine, etc., for example
[0069] According to this invention, the partial amine salt of said P-monomer can make an amine able to act on P-monomer, and can be obtained as mixture with P-monomer which carried out amine chlorination with P-monomer which has not carried out amine chlorination so that the ratio R of P-acid radical which the amino group / P-monomer of an amine have may be preferably set to $0< R<1$. As for especially the ratio R of P-acid radical which the amino group / P-monomer of an amine have in the partial amine salt of P-monomer according to this invention, it is desirable that it is the range of $0.1<=R<=0.9$.
[0070] However, according to this invention, the amine chlorination of all the P-monomers is carried out, this amine chlorination P-monomer and P-monomer which has not carried out amine chlorination can be mixed, and this can also be made into the partial amine salt of P-monomer. therefore, P-monomer which has not carried out amine chlorination in this case with P-monomer which carried out amine chlorination -- setting -- each P-monomer -- being the same -- you may differ.
[0071] According to this invention, in this way, the proton conductivity film makes base material porous membrane support preferably the partial amine salt of P-monomer, P-monomers, such as a polyfunctional P-monomer, a polyfunctional un-P-monomer, and a single functionality un-P-monomer, and P-salt monomer mentioned above if needed, and the monomer which has copolymerization nature, and thermal polymerization, photopolymerization, etc. should just carry out the polymerization of the above-mentioned

monomer by the proper approach learned from before. However, as a polymerization method, a photopolymerization method is simple and those with insurance and a deer ca[illegible]o obtain the partial amine salt of P−polymer especially in a short time. Moreover, after performing photopolymerization, in order to carry out the polymerization of the residual monomer if needed, photopolymerization and thermal polymerization may be further performed more at an elevated temperature.

[0072] What is known conventionally should just be suitably used for the above−mentioned photopolymerization initiator. For example, the 2−benzyl−2−dimethylamino−1−(4−morpholino phenyl) butanone −1 (Ciba−Geigy IRUGA cure 369), the 2−methyl−1−[4−(methylthio) phenyl]−2−morpholino propanone −1 (Ciba−Geigy IRUGA cure 907), 1−hydroxy cyclohexyl phenyl ketone (Ciba−Geigy IRUGA cure 184), benzyl dimethyl ketal (Ciba−Geigy IRUGA cure 651), etc. can be used. Even if it uses light with a wavelength of 300nm or more, especially the thing in which a polymerization is possible is desirable. Such a photopolymerization initiator is usually added about 0.01 to 5% of the weight to the whole monomer containing the partial amine salt of P−monomer.

[0073] What is necessary is to immerse porous membrane in this mixture, and just to apply this mixture to base material porous membrane, for example, in order to make the partial amine salt of P−monomer, and the mixture which contains a copolymerization nature monomer, a photopolymerization initiator, etc. of said others if needed support in the hole of porous membrane.

[0074] Thus, it makes it face that porous membrane supports the mixture containing the partial amine salt of P−monomer, or it, and the viscosity of the mixture containing this P−monomer partial amine salt and it may be adjusted suitably. namely, a polymer proper in carrying out precuring of a part of partial amine salt of P−monomer, in order to raise viscosity −− small quantity −− you may make it add and dissolve On the contrary, a suitable solvent may be added and diluted in order to lower viscosity.

[0075] Thus, after making the mixture which contains the partial amine salt of P−monomer, and this in porous membrane support, porous membrane is pinched with the mold releasing film made of polyester resin, and this exchange film is intercepted from oxygen (therefore, air), The proton conductivity film which makes the copolymerization nature monomer of the partial amine salt of P−monomer or others come to support the partial amine salt of P−polymer in the hole of porous membrane Mitsuteru putting and by carrying out photopolymerization using a high−pressure mercury lamp etc. can be obtained.

[0076] An optical exposure required for the above−mentioned photopolymerization is usually 0.1 − 5 J/cm2, although it changes with systems. Extent is enough. Photopolymerization is usually performed near a room temperature, in order to make high molecular weight of the partial amine salt of P−polymer obtained, but in order to raise conversion, it may perform photopolymerization at higher temperature. Moreover, it is low temperature at first and, subsequently you may photopolymerize at an elevated temperature.

[0077] Moreover, as an option, the proton conductivity film by this invention carries out the polymerization of the P−monomer to having mentioned above in the hole of porous membrane similarly, makes P−polymer generate, can make an amine able to act and, subsequently to this P−polymer, can be obtained also by amine−izing a part of that P−acid radical. According to this invention, an amine is made to act on P−polymer and an amine is made to act on P−polymer so that the ratio R of P−acid radical which the amino group / P−polymer of an amine have in this case may be set to $0 < R < 1$, and the ratio R of P−acid radical which the amino group / P−polymer of an amine have may be preferably set to $0.1 <= R <= 0.9$.

[0078] Thus, also when carrying out the polymerization of the P−monomer in the hole of porous membrane and making P−polymer generate, a polyfunctional P−monomer and a polyfunctional un−P−monomer can be used if needed, and P−polymer which has the structure of cross linkage can be made to be able to construct a bridge like the case where the polymerization of the partial amine salt of P−monomer is carried out, and a copolymer with that can be made to generate using a monofunctional nature P−monomer.

[0079] In case monomer mixture with the monomer of said others which have copolymerization nature in these is infiltrated into porous membrane the partial amine salt of P−monomer or P−monomer, and if needed according to this invention, when the ratio (filling factor) with which the above−mentioned monomer mixture fills up the hole of porous membrane is low, it has the vesicular structure in which, as for base material porous membrane, after the polymerization of the above−mentioned monomer has permeability. In this way, the proton conductivity porous membrane which has permeability (carrying out the amine chlorination of the P−acid radical of generated P−polymer in being required) can be obtained. On the other hand, when the above−mentioned filling factor is high, after the polymerization of the above−mentioned monomer, the hole is blockaded substantially and base material porous membrane can obtain the proton conductivity nonporous film without permeability (carrying out the amine chlorination of the P−acid radical of generated P−polymer, in being required). As a temporary standard, if the filling factor of a monomer is 80% or more, the proton conductivity nonporous film without the permeability which comes to blockade the

hole of base material porous membrane substantially can be obtained.
[0080] In this invention, it the mo[illegible]r mixture with the partial amine salt o[illegible]onomer, P-monomer, and the monomer of the above which h[illegible]copolymerization nature in these, and o[illegible]s is not only filled up with the hole of base material porous membrane, but may cover a part of one [at least] front face [at least] of base material porous membrane. In this case, the filling factor of the above-mentioned monomer mixture exceeds 100%. Thus, if base material porous membrane is made to support monomer mixture with the filling factor exceeding 100% and an optical exposure is carried out at this, it porous membrane is not only filled up with the polymer which the hole generates, but can obtain the proton conductivity film by which a part of one [at least (carrying out the amine chlorination of the P-acid radical of generated P-polymer, in being required)] front face [at least] was covered by the polymer.
[0081] furthermore, the opening of the remainder of the hole which the proton conductivity film obtained by doing in this way has according to this invention -- that is, do in this way The opening which remains on the obtained proton conductivity film can be heated and shrunk, or the proton conductivity nonporous film which blockades a part of above-mentioned opening [at least] which remains on the proton conductivity film with a means suitably, such as carrying out melting, can consider as a proton conductivity film, blockades all of heating and the opening which remains on the proton conductivity film especially preferably, and does not have permeability can be obtained. Moreover, a part of opening which remains on the proton conductivity film is blockaded if needed, and a proton conductivity perforated film with permeability can be obtained.
[0082] Thus, the proton conductivity film and proton conductivity film of P-polymer which make it come to support a partial amine salt in the hole of base material porous membrane have high proton conductivity. The film and film which have high proton conductivity can be obtained, so that according to this invention the filling factor of the monomer mixture containing the partial amine salt of P-monomer to porous membrane or this is made high and the filling factor of the partial amine salt of P-polymer to the hole which porous membrane has is made high.
[0083] According to this invention, the proton conductivity film of nonporous structure can be obtained the proton conductivity film which has a vesicular structure and has permeability in this way, the proton conductivity film which can obtain the proton conductivity film of nonporous structure, and has a vesicular structure on the contrary, and has permeability, and reversely. For example, permselectivity charged membrane etc. can use preferably the proton conductivity film which has a vesicular structure and has permeability, and a film for the application which harnessed the opening.
[0084] However, the proton conductivity film and film which have a vesicular structure and have permeability have problems, like cross leak of gas tends to take place, if it uses as a separator for fuel cells. Therefore, it is desirable to use the proton conductivity nonporous film which comes to blockade all the openings that remain on the proton conductivity film with heating and proper means, such as to carry out melting, as the proton conductivity nonporous film which filled up the hole of porous membrane with the partial amine salt of P-polymer altogether substantially as mentioned above was used for such an application and proton conductivity porous membrane was mentioned above.
[0085] The proton conductivity film and proton conductivity film by this invention, The proton conductivity polymer which consists of a partial amine salt of P-polymer is compound-ized to porous membrane. Preferably While infiltrating the partial amine salt of P-monomer into porous membrane, carrying out a polymerization in the hole of this porous membrane and making the partial amine salt of P-polymer generate The partial amine salt of this P-polymer is made to support in the hole of the above-mentioned porous membrane, and porous membrane and the partial amine salt of P-polymer are unified.
[0086] Therefore, according to this invention, it originates in compound-ization with base material porous membrane and a proton conductivity polymer, and the proton conductivity film or film which is various points and was excellent can be obtained. For example, in addition to the high proton conductivity originating in the partial amine salt of P-polymer, the proton conductivity film or film which has a high mechanical strength and the outstanding handling nature can be obtained by using the tough porous membrane which consists of ultra high molecular weight polyethylene etc. as a base material.
[0087] Especially, according to this invention, the partial amine salt of P-monomer is made to support in the hole of porous membrane, a polymerization is carried out, and the partial amine salt of P-polymer is united with base material porous membrane, The polymer chain of the partial amine salt of P-polymer can be twined around the mesh of porous membrane at altitude. Further If copolymerization of a polyfunctional P-monomer or the polyfunctional un-P-monomer is carried out with the partial amine salt of P-monomer Physical association arises by the polymer network as for which the partial amine salt of P-polymer which constructed the bridge, and the polymer chain which constitutes porous membrane carried out mutual

penetration, and the proton conductivity film and film which strengthened the adhesion of a proton conductivity polymer and porous membrane further can be obtained in this way.

[Translation done.]

EXAMPLE

[Example] Although an example is given to below and this invention is explained to it, this invention is not limited at all by these examples. Moreover, the property of the porous membrane used for below and the property of the obtained proton conductivity film or a film were evaluated as follows.
[0089] (Thickness of the film or a film) It measured by 1/10000 thickness gage.
(Void content of porous membrane) It computed by the bottom formula from weight [of per an unit area S (cm2)] W (g) of porous membrane, average thickness t (micrometer), and a consistency d (g/cm3).
[0090] Void content (%) = (1-(104 and W/(S-t-d)) x100[0091]) After leaving it for 4 hours under the environment which adjusted the proton conductivity film or a film to the temperature of 25 degrees C, and 50% of relative humidity, (Proton conductivity) Hewlett Packard LCR meter HP4284A is used. The sample of 1cm angle of given thickness Mino was inserted between platinum electrodes, it measured by the complex impedance method under conditions of the temperature of 25 degrees C, and 50% of relative humidity, and proton conductivity was computed using the resistance of the real part when extrapolating to the resistance zero of imaginary part.
[0092] (Rate of volume filling of the partial amine salt of P-polymer to the hole of base material porous membrane) It computed by the bottom formula from weight [of the volume V of base material porous membrane (cm3), void content / of base material porous membrane / phi, and the partial amine salt of (%) and P-polymer] M (g), and the consistency d of the partial amine salt of P-polymer (g/cm3).
[0093] Filling factor (%) =104 and M/(V-phi-d)
[0094] (Tensile strength) About the test piece (based on the No. 1 form test piece in JIS K 7113 and the tension test approach of plastics) pierced in the dumbbell mold, it measured using the tension tester (autograph AGS[by Shimadzu Corp.]-50D).
[0095] An example 1 70 % of the weight (light ester P-1 made from Kyoeisha Chemistry M) of P-monomers which consist of 2-methacryloiloxy-ethyl phosphate / screw (methacryloiloxy-ethyl) diphosphate (65 / 35 mole ratios) (Preparation of the partial amine salt of P-monomer) Stirring in the monomer mixture 100 weight section which consists of 30 % of the weight of methoxy ethyl acrylate The diethanolamine of the calculated requirements was added gradually beforehand and the monomer mixture which consists of the partial amine salt and methoxy ethyl acrylate of P-monomer of a phosphoric-acid radical of ratio R=1/2 was obtained. [of diethanolamine] [of the amino group / P-monomer]
[0096] (Manufacture of the proton conductivity film) The benzyl dimethyl ketal (Ciba-Geigy IRUGA cure 651) 0.25 weight section and the 1-hydroxy cyclohexyl phenyl ketone (Ciba-Geigy IRUGA cure 184) 0.25 weight section were dissolved in the above-mentioned monomer mixture 100 weight section.
[0097] It is weight average molecular weight 1.0x106 as it is, without diluting this. It applied to both sides of the porous membrane T1 (micrometers [of thickness / 25],% [of void contents / 40], 0.10 micrometers of average apertures) which consists of ultra-high-molecular-weight-polyethylene resin, and was made to sink into the hole of porous membrane.
[0098] Thus, the processed porous membrane is pinched with the mold releasing film made of polyester resin. The optical irradiation equipment (UB 021-1 made from Eye Graphic B-13) equipped with the high-pressure mercury lamp after intercepting porous membrane from air is used, and it is energy 1.5 J/cm2 to the above-mentioned porous membrane. An optical exposure is carried out. While carrying out photopolymerization of the above-mentioned monomer mixture in the hole and making the copolymer of the partial amine salt of P-polymer, and methoxy ethyl acrylate generate, this was made to support in the hole of the above-mentioned porous membrane, and the proton conductivity film F1 with a thickness of 40 micrometers was obtained. In this proton conductivity film, the hole of porous membrane is completely filled up with the copolymer of the partial amine salt of the above-mentioned P-polymer, and methoxy ethyl

acrylate, and both the front faces of porous membrane were also covered with the layer of the above-mentioned copolymer.
[0099] The proton conductivity of [redacted]bove-mentioned proton conductivity [redacted]1 was 2.3x10-3 S/cm, and tensile strength was 75MPa(s).
[0100] (Fuel cell) It is a platinum catalyst 0.6mg/cm 2 The above-mentioned proton conductivity film F1 was inserted between two carbon paper which the front face was made to support with a rate, it joined using the hotpress, and the film-electrode zygote (MEA) was manufactured.
[0101] The fuel cell property of Above MEA was evaluated using the fuel cell evaluation equipment by TOYO Corp. The back-pressure valve was not extracted but the pressure was performed in ordinary pressure. Humidifier temperature was made into 70 degrees C the 80-degree-C and oxygen side the hydrogen side, and fuel cell cel temperature was made into 70 degrees C. When the current-electrical-potential-difference (I-V) curve was obtained by the Tafel method, the current-electrical-potential-difference (I-V) curve almost equivalent to the case where Nafion (trademark) 117 film is used for a result as proton exchange film as shown in drawing 1 was obtained. That is, the proton conductivity film by this invention has a fuel cell property equivalent to Nafion 117 film.
[0102] Stirring in the P-monomer 100 weight section which consists of the same 2-methacryloiloxy-ethyl phosphate as example 2 (preparation of the partial amine salt of P-monomer) example 1, and screw (methacryloiloxy-ethyl) diphosphate, the powder of the imidazole of the calculated requirements was added gradually beforehand, and it considered as the partial amine salt of P-monomer of ratio R=1/3 of the phosphoric-acid radical of the amino group / P-monomer of an imidazole.
[0103] (Manufacture of the proton conductivity film) The benzyl dimethyl ketal (it is the same as the above) 0.25 weight section and the 1-hydroxy cyclohexyl phenyl ketone (it is the same as the above) 0.25 weight section were dissolved in the partial amine salt 100 weight section of the above-mentioned P-monomer.
[0104] The porous membrane T1 which consists of the same ultra-high-molecular-weight-polyethylene resin as an example 1 is carried on the mold releasing film made of polyester resin, without diluting the partial amine salt of the above-mentioned P-monomer, as it is, it applied to the exposure front face of porous membrane, it drew through on it with the bar, the excessive monomer was removed on it from the front face of porous membrane, and the partial amine salt of the above-mentioned P-monomer was infiltrated into it only all over the hole of porous membrane.
[0105] Thus, the mold releasing film made of polyester resin is put also on the exposure front face of the processed porous membrane, porous membrane is intercepted from air, the same optical irradiation equipment as an example 1 is used, and it is energy 1.5 J/cm2. An optical exposure is carried out at porous membrane. While carrying out photopolymerization of the partial amine salt of the above-mentioned P-monomer in that hole and making the partial amine salt of P-polymer generate, the partial amine salt of this P-polymer was made to support in the above-mentioned hole, and the proton conductivity film F2 with a thickness of 25 micrometers was obtained. In this proton conductivity film, the hole of porous membrane was completely filled up with the polymer. The proton conductivity of this proton conductivity film F2 was 1.2x10-3 S/cm.
[0106] Stirring in the P-monomer 100 weight section which consists of the same 2-methacryloiloxy-ethyl phosphate as example 3 (preparation of the partial amine salt of P-monomer) example 1, and screw (methacryloiloxy-ethyl) diphosphate, the aniline of the calculated requirements was added gradually beforehand and it considered as the partial amine salt of P-monomer of ratio R=1/5 of the phosphoric-acid radical of the amino group / P-monomer of an aniline.
[0107] (Manufacture of the proton conductivity film) The benzyl dimethyl ketal (it is the same as the above) 0.25 weight section and the 1-hydroxy cyclohexyl phenyl ketone (it is the same as the above) 0.5 weight section were dissolved in the partial amine salt 100 weight section of the above-mentioned P-monomer, and this was diluted with the methanol so that the partial amine salt concentration of P-monomer might become 30 % of the weight. It diluted.
[0108] Porous membrane T2 (40 micrometers of thickness) which consists of ultra-high-molecular-weight-polyethylene resin of weight average molecular weight 2.4x106 44% of void contents and 0.15 micrometers of average apertures are carried on the mold releasing film made of polyester resin. The diluted solution of the partial amine salt mixture of the above-mentioned P-monomer is applied, it draws through with a bar, and an excessive monomer is removed from the front face of porous membrane, it was air-dry on the exposure front face of this porous membrane, and the partial amine salt of the above-mentioned P-monomer was infiltrated into it only all over the hole of porous membrane.
[0109] Thus, the mold releasing film made of polyester resin is put also on the exposure front face of the

processed porous membrane, porous membrane is intercepted from air, the same optical irradiation equipment as an example 1 is used, and it is energy 1.5 J/cm2. An optical exposure is carried out at porous membrane. While carrying out photopolymerization of the above-mentioned monomer mixture in that hole and making the partial amine salt of P-polymer generate, the partial amine salt of this P-polymer was made to support in the above-mentioned hole, and the proton conductivity film F3 with a thickness of 40 micrometers was obtained. In this proton conductivity film, the hole of porous membrane was partially filled up with the partial amine salt of P-polymer. The proton conductivity of this proton conductivity film F3 was 8.5x10-5 S/cm.

[0110] In example of comparison 1 example 1, the monomer mixture containing the partial amine salt of the P-monomer same on the mold releasing film made of polyester resin as an example 1 was applied to the layer with a thickness of 40 micrometers, without using base material porous membrane.

[0111] The mold releasing film made of polyester resin is carried also on this spreading layer, the spreading layer of the partial amine salt of the above-mentioned monomer mixture is intercepted from air, the same optical irradiation equipment as an example 1 is used, and it is energy 1.5J/cm2. Carried out the optical exposure, the copolymer of the partial amine salt of P-polymer and methoxy ethyl acrylate was made to generate, and the proton conductivity film R1 with a thickness of 40 micrometers it is thin only from this copolymer was obtained. The proton electric conductivity of this proton conductivity film was 2.6x10-3 S/cm, and tensile strength was 9MPa.

[0112] After having carried out the ion exchange of the water solution (poly eggplant PS[by TOSOH CORP.]- 5) of example of comparison 2 sodium polystyrene sulfonate using strong acid nature cation exchange resin, changing sodium salt into the free acid and condensing this, it was made to dissolve in a methanol and the methanol solution of the polystyrene sulfonate of concentration was prepared 20%.

[0113] The porous membrane T2 which consists of the same ultra-high-molecular-weight-polyethylene resin as an example 3 was put on the mold releasing film made of polyester resin, the methanol solution of the above-mentioned polystyrene sulfonate is applied to the exposure front face, it was dried, and the proton conductivity film R2 with a thickness of 58 micrometers was obtained.

[0114] In this proton conductivity film, the hole of porous membrane is completely filled up with the above-mentioned polystyrene sulfonate, and the front face by the side of spreading of the above-mentioned polystyrene sulfonate of porous membrane was also covered with the layer of polystyrene sulfonate. The proton conductivity of this proton conductivity film R2 was 2.0x10-5 S/cm.

[0115] When gas conditioning of this proton conductivity film was again carried out to the temperature of 25 degrees C, and 50% of relative humidity after being immersed to this water as a result of eluting a part of polystyrene sulfonate underwater, when immersed in water for 24 hours, and proton conductivity was measured, it was 3.7x10-6 S/cm.

[Translation done.]

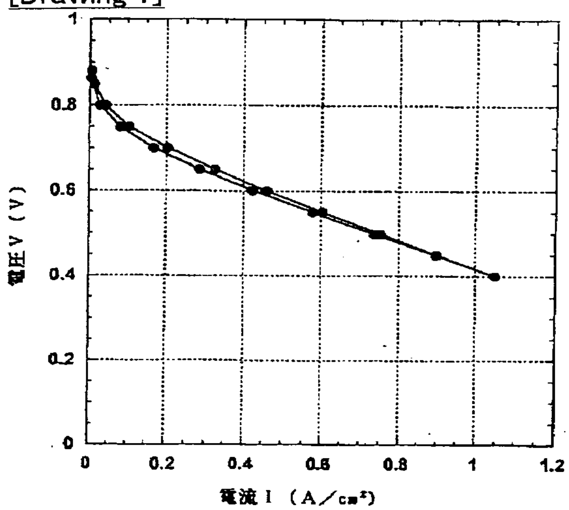
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Tafel which shows the fuel cell property of the film-electrode zygote (MEA) prepared using the proton conductivity film by ** and this invention -- it is a current-electrical-potential-difference (I-V) curve by law.

[Translation done.]

DRAWINGS

[Drawing 1]



[Translation done.]